AOSTRA TECHNICAL PUBLICATION SERIES #5

A REVIEW OF ANALYTICAL METHODS FOR BITUMENS AND HEAVY OILS

THE ALBERTA COMMITTEE ON OIL SANDS ANALYSIS

Alberta
OIL SANDS TECHNOLOGY
AND RESEARCH AUTHORITY

A REVIEW OF ANALYTICAL METHODS FOR BITUMENS AND HEAVY OILS

THE ALBERTA COMMITTEE ON OIL SANDS ANALYSIS
EDMONTON, ALBERTA, CANADA

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Published by

Alberta
OIL SANDS TECHNOLOGY
AND RESEARCH AUTHORITY

92-04027/

PUBLISHER'S NOTE

AOSTRA TECHNICAL PUBLICATION SERIES
NUMBER 5

AOSTRA is pleased to publish this fifth book in a series of special publications by industry and academic authors. Like its predecessors *"Syncrude Analytical Methods for Oil Sand and Bitumen Processing"*, *"The Thermodynamic and Transport Properties of Bitumens and Heavy Oils"*, *"Aquathermolysis: A Synopsis of Work on the Chemical Reaction Between Water (Steam) and Heavy Oil Sands During Simulated Steam Stimulation" and "Oil Sands Composition and Behavior Research"*, this publication is designed to make available, research results, analytical procedures, and engineering data on the properties and behaviour of Alberta petroleum resources that may otherwise not be available to the public.

Alberta Oil Sands Technology
and Research Authority

Edmonton, Alberta

January 1988

PREFACE

"A man with one watch knows the time; a man with two is never sure."

Anon

Analysts, when faced with unacceptable variations in analytical data, sometimes attempt to correct the situation by adopting a referee method. History has proven that this tactic is not generally successful, because there is rarely sufficient scientific justification for identifying one method as being superior to all others for all samples. Systematic differences between analysts and laboratories do exist even when all are using the same analytical method. Although I may have wished at one time to offer through this book, a collection of referee methods, it rapidly became clear that an understanding of the limitations of the numerous methods for analyzing bitumens and heavy oils was preferred. I hope that this book fills that need.

In the interest of keeping the Reference section of each chapter to a reasonable length, detailed references to the following were not provided:

> Annual Book of ASTM Standards, published by the American Society of Testing and Materials, 1916 Race St., Philadelphia, PA, 19103.
>
> IP Standards for Petroleum and Its Products, published by Heyden and Son Inc., 247 South 41st St., Philadelphia, PA, 19104.
>
> Syncrude Analytical Methods for Oil Sand and Bitumen Processing, published by the Alberta Oil Sands Technology and Research Authority, 5th Floor, 10010 - 106 St., Edmonton, Alberta, T5J 3L8.
>
> UOP Laboratory Test Methods for Petroleum and Its Products, Signal UOP, 20 UOP Plaza, Algonquin and Mt. Prospect Roads, Des Plaines, Illinois, 60016.
>
> Alberta Committe on Oil Sands Analysis. Bitumen Round Robin (sic) No. 2, available from AOSTRA Library and Information Services, 5th Floor, 10010 - 106 St., Edmonton, Alberta, T5J 3L8 (ALIS #09037).

In addition, this review uses extensively the data collected by Phillips Petroleum Co., Bartlesville, Oklahoma during a cooperative study in 1984. I am grateful to John Paxon who released the data to us. The Analytical Services group in the Oil Sands Research Department and the Gasoline and Oil Testing Laboratory, both at the Alberta Research Council, and the Spectral Services Laboratory in the Department of Chemistry at the University of Alberta promptly provided data that addressed aspects of some analytical methods that had not previously been reported in the open literature.

The contributors, whose names appear at the beginning of each chapter, and the assistant editors played important roles in providing and organizing the information that they had collected within their own organizations. The translators (Koichi Takamura, Dagmar Losert, Eva Miles-Dixon, Lavorka Sevenson and Mario De Rocco) and background researchers (Deborah Henry, Helen Helm and Leslie Rawluk) were instrumental in finding information in the open literature that would otherwise have been overlooked. Wendy Zwickel, my style guide and grammatical consultant, and Kelly Cymbala who skillfully typed numerous versions of the manuscript were especially helpful.

The Alberta Oil Sands Technology and Research Authority provided the financial support for the preparation and publication of this book.

I thank everyone who contributed.

Dean Wallace
Editor

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Chapter 1: INTRODUCTION

INTRODUCTION

Analytical methods used to describe conventional oils must be modified for the characterization of heavy oils and bitumens in the same way that conventional production techniques have been modified or replaced by new techniques for recovering petroleum from heavy oil and oil sand deposits. As analytical properties of minor interest in the conventional oil industry can be important when monitoring the recovery and upgrading of heavy oils and bitumens, development of an acceptable analytical method often begins with identification of the property requiring measurement. Next, research into methods for the measurement of properties of interest is conducted, often independently in numerous laboratories, resulting in the development of a variety of methods. Each reflects the background of the investigator, his ability to interpret the results in relation to the application, the analytical facilities available and the required levels of accuracy, precision, speed and cost. Then, it is sometimes found that not all methods give equivalent results. Finally, through a concerted reviewing process, deficiencies are identified, promising methods are improved and acceptable methods are adopted.

In 1979, representatives of industry, government and the universities, interested in resolving analytical problems, formed the Alberta Committee on Oil Sands Analysis (ACOSA) as a forum for the exchange of information, discussion of problems and cooperative development of analytical methods. ACOSA set the following goals to meet this blanket objective:

- evaluation of existing methods by identifying their limitations and applicability
- upgrading or improvement of existing analytical methods
- development of new analytical methods
- standardization of analytical methods and adoption of recommended methods where applicable or desirable
- development of recommended methods for sampling, sample storage and sample preparation.

During the six years which followed, ACOSA sponsored several cooperative studies on the measurement of properties of oil sands, bitumens and heavy oils. These studies showed that:

- several methods are often available for the measurement of a given property
- some methods are more appropriate than others
- not all methods provide equivalent data
- laboratories using the same method do not always report equivalent data for a given sample
- in some analyses, the error in sampling and subsampling is greater than the error in the measurement.

The exact steps followed in the analysis of a sample depends, among other factors, on the analyst's personal interpretation of the written word and unique characteristics of the test sample. A single standard method for conventional oil can therefore be the forerunner of several similar but distinct methods for bitumen. This book attempts to explain variations in the data from cooperative studies on the analysis of bitumen and heavy oils by reviewing the open literature and unpublished data provided by many companies. It should help analysts to choose appropriate analytical methods and make users of data more aware of the reliability and pertinence of the measurements to the problem they are trying to resolve.

This book should be viewed as the first in a series. Successive editions will be expanded to incorporate new data and methods, particularly in the analysis of whole oil sand, oil sand solids and separation of compound classes.

Chapter 2: SAMPLING

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SAMPLING

The reliability of any analytical measurement depends on the quality of the sample. A poorly devised sampling plan may make the analytical results unreliable or even impossible to interpret. This consideration is especially important when addressing the problem of sampling bulk materials such as oil sand that may be highly heterogeneous.

The design of bulk sampling programs involves:

- identification of the population from which the sample is to be obtained
- selection and withdrawal of valid samples of this population
- reduction of each bulk sample to a laboratory sample suitable for the analytical techniques to be used.

A brief list of definitions commonly used is provided in the Glossary.

Few industry-wide methods exist for sampling and subsampling. This is in contrast with analytical methods, many of which are drawn from procedures prepared by the Institute of Petroleum, the American Society for Testing and Materials, or collections of companies' methods (UOP, Syncrude Canada Ltd., and others). There are several reasons for the scarcity of standardized sampling methods. First, for materials as heterogeneous as oil sand and bitumen, the required quality of the data controls the sampling protocol. Whereas it may suffice to collect two or three increments to determine whether the sulfur content of a bitumen is closer to 1% or 5%, many more increments would need to be collected from a feedstock to close sulfur balances around an upgrading process.

Second, the sampling protocol which will hold sampling uncertainty for a property to a given level depends upon the form of the material being tested. When determining the reserves in a lease, both vertical and horizontal variability must be considered. In a stockpile or windrow, some of the segregation apparent in the formation is lost due to mixing during mining. The number of increments required will therefore be reduced compared to an equal volume of undisturbed oil sand. Provision must still be made however for collection of surface and subsurface samples. In small pilot-scale projects, protocols can be developed for collection of samples from a stockpile or conveyor belt for subsequent laboratory analysis. On a commercial scale, continuous sampling and measurement is required for precise estimates of feedstock grade. In these four situations, the same component (bitumen) in the same matrix (oil sand) is being analyzed but sampling protocols vary considerably.

Third, sampling and subsampling methods are often specific to the material being analyzed. For example, 45-gallon drums of Suncor coker feed bitumen and Lloydminster heavy oil being analyzed for many hydrocarbon properties, can be mixed by extensive rolling on a drum roller. Syncrude coker feed and Grosmont Formation bitumens are so viscous that they must be heated and mixed with a powerful propeller-type stirrer. While rolling of a Lloydminster oil might provide adequate homogeneity for, say, an asphaltene measurement, it would be necessary to use a recirculation loop and a static mixer if BS&W were to be determined. Clearly, any attempt to identify a sampling protocol for every conceivable situation would be fruitless. In this chapter, we present some fundamental rules of sampling with appropriate references so analysts can develop their own protocols based upon scientific and statistical principles.

PRELIMINARY CONSIDERATIONS IN SAMPLING

Many of the sources of error in an analysis, such as contaminated reagents, biased methods, or operator errors, can be controlled by proper use of blanks, standards, and reference samples. Neither control nor blank will avail, however, if the sample is invalid. Accordingly, sampling uncertainty is often treated separately from other uncertainties. For random errors the overall standard deviation, s_o, is related to the standard deviation for the sampling operation, s_s and to that for the remaining analytical operations, s_a by

$$s_o^2 = s_a^2 + s_s^2 \qquad (1)$$

Whenever possible, measurements should be conducted so that sample variability and measurement variability can be evaluated separately. For a measurement process in statistical control where s_a is known, s_s can be evaluated from s_o found by analysis of the samples. Otherwise, a series of replicate measurements or samples can be taken to evaluate both standard deviations.

Youden points out that further reduction in analytical uncertainty is unimportant once it is one-third or less of the sampling uncertainty.[16] Therefore, if the sampling uncertainty is large and cannot be reduced, a rapid, approximate analytical method may be sufficient and further refinements in measurement will improve precision only slightly.

Consider the case of sampling a 100-ton stockpile of Athabasca oil sand to determine its average bitumen content. A sampling uncertainty s_s, of approximately 1% is associated with collection of a single 120-g test portion and the analytical uncertainty, s_a, is approximately 0.15%.[12,13] Therefore, the overall uncertainty, s_o, in a single data point is $(1^2 + 0.15^2)^{1/2} = 1.0\%$. Use of either a more precise analytical method for which $s_a = 0.0$ or a less precise method with $s_a = 0.3$ would not affect the precision of an analysis. Precision would be improved by collecting n increments to reduce s_s by a factor of $(n)^{1/2}$. In this application, the incentive for changing the analytical method revolves around either improvement in the accuracy of the method, or reduction in cost and analysis time.

Even if the analytical uncertainty is relatively large compared to sampling and subsampling uncertainty, a reduction in analytical uncertainty does not always yield as much benefit as might be presumed at first glance. Sampling, subsampling and analytical uncertainties of 3, 3 and 6 kg/m^3 were estimated in one set of experiments for determination of density of bitumen by displacement.[11] The overall uncertainty in a single analysis was $(3^2 + 3^2 + 6^2)^{1/2}$ or 7 kg/m^3. Had a pycnometer method with an analytical uncertainty of 3 kg/m^3 been used instead of the displacement method, the overall uncertainty in a single analysis would have been 5 kg/m^3. On the basis of this information, the analyst in consultation with the data user, can decide whether the extra labor required for the pycnometer method (one hour rather than twenty minutes) is justified by the slight improvement in overall precision. Estimates of variability in different stages of various analyses are provided throughout this book.

TYPES OF SAMPLES

Random Samples. Like statisticians, analytical chemists ordinarily wish to generalize from a small body of data to a larger body of data. Rarely are they interested only in the specimen/sample actually examined; most frequently they want the characteristics of the population. Obviously, if the samples under examination are biased, any inferences made from them will likewise be biased.

Statisticians carefully distinguish the target population to which we would like our conclusions to apply and the parent population from which samples were actually drawn. In practice these are rarely identical, although the difference may be small. This difference may be minimized by random selection of portions for examination, in which each part of the population has an equal chance of selection. From such random samples, generalizations based on mathematical probability can be made.

Random sampling is difficult. A sample selected haphazardly is not a random sample. It can be difficult to convince untrained individuals who obtain samples that an apparently unsystematic collection pattern must be followed closely to be valid. On the other hand, samples selected by a defined protocol may reflect bias inherent in the protocol. Even under the most favorable circumstances, unconscious selection and biases can occur.

Whenever possible, the use of a table of random numbers[6] is recommended for sample selection. The bulk material is divided into a number of real or imaginary segments. For example, an oil sand deposit, or a portion of it, can be conceptually subdivided into cells, horizontally if lateral variability is of interest, or vertically if a mining face is under study. Each segment is then assigned a number. Segments from which sample increments will come are selected by starting in an arbitrary place in a random number table and choosing numbers according to a predecided pattern, such as adjacent, alternate, or nth entries, and sampling those segments for the predetermined number of samples.

Because of its simplicity, sampling at evenly spaced intervals over the bulk is often used in place of random sampling. If it is used, a random starting point should be selected, and the results should be closely monitored to prevent errors from periodicity in the material.

Systematic samples. Samples are sometimes collected in a systematic manner and analyzed to reflect or test some systematic hypothesis, such as changes in composition with time, temperature, or spatial location. Each set may be considered to represent a separate, discrete population under the existing conditions. Results may therefore be statistically tested for the significance of any apparent differences.

A carefully designed sampling plan takes into consideration the possible concurrence of unanticipated events or phenomena that could prejudice the analyses. For example, measurements at timed intervals are sometimes made with a random start or other superimposed random time element. Needless to say, the less that is known about a given process, the more randomness is merited. Conversely, the more fully a process is understood, the more efficient is a systematic approach to data acquisition.

Representative samples. In analytical discussions "representative sample" frequently connotes a single sample of a universe or population (e.g., oil sand pile, tailings pond, groundwater) expected to exhibit average properties of the population. It is not possible to select such a sample by a random process, or to verify its representativeness.

While it may reduce costs, the analysis of a single sample defined as representative yields information not on a par with that from valid random samples of the population, except when a vigorous effort is exerted to homogenize the population prior to sampling. Because of the difficulties in selecting or producing a single "representative sample," this concept is discouraged for general purposes and reserved for cases where the effort required is justified. Furthermore, much compositional information is lost. A properly designed and executed random sampling plan yields sample mean and variation between members, neither of which can be obtained by measurement of one "representative sample."

Composite samples. A composite sample may be considered a special way of producing a representative sample. Many sampling procedures assume only average composition is desired, such as bulk, time-weighted, or flow-proportional averages. In such cases collection of a composite is appropriate. Elaborate crushing, grinding, mixing, and blending procedures for preparing solid composites, and various sampling systems to obtain liquid (especially water) composites, have been developed and even standardized.

Analysis of individual samples permits determination of the average (at the expense of extra analytical effort), of the distribution of samples within the population (between-sample variability), and of within-sample variability. All of this information is necessary for cooperative test samples and in reference material usage, especially when apparent differences within and between laboratories need to be evaluated. Composite samples provide only limited information. The consequences of compositing should be carefully considered before deciding between this approach and the analysis of individual samples.

Subsampling. Subsampling is necessary when the sample received by the analytical laboratory is larger than that required for a single measurement. Test portions taken for replicate measurements or for measurement of different constituents by several techniques must be sufficiently alike so the results are comparable. The effort necessary to reduce particle size, and to mix or otherwise process the laboratory sample before withdrawing portions (subsamples) for analysis depends on the homogeneity of the original sample. In general, the subsampling standard deviation should not exceed one-third of the overall sampling standard deviation. Although this may sound appreciable, it is wasteful of time and effort to decrease it below this level. Care should be taken to avoid introducing segregation into an already homogenous sample during subsampling. Even though analysts may not collect the sample, they should be provided with any available information on the homogeneity of the samples received and have sufficient knowledge of sampling theory to obtain the subsample properly.

A method for estimating the amount of sample required in a given increment so as not to exceed a predetermined sampling uncertainty has been provided by Ingamells.[4,5] Based on the knowledge that the between-sample standard deviation s_s decreases as the sample size

Table 2.1: Determination of Segregation in a Laboratory Sample of Oil Sand[a]

	Mean sample weight, w (g)	R^2	Best-fitting line $R^2 = \frac{m}{w} + b$	
			m	b
Bitumen	11.832	8.316	91.53 ± 8.01	0.36 ± 0.40
	21.696	4.225		
	45.031	2.125		
	101.381	1.675		
Water	11.832	1419.94	18802 ± 1152	−200 ± 57
	21.696	617.26		
	45.031	176.75		
	101.381	45.05		
Solids	11.832	2.118	28.68 ± 2.23	−0.35 ± 0.11
	21.696	0.901		
	45.031	0.182		
	101.381	0.052		

is increased, Ingamells has shown that the following relation is valid for subsampling well-mixed laboratory samples:

$$wR^2 = K_s \qquad (2)$$

where w represents the average test portion weight, R is the relative standard deviation (in percent) of sample composition, and K_s is a sampling constant, corresponding to the weight of sample required to limit the sampling uncertainty to 1% with 68% confidence. K_s may be determined by estimating s_s from a series of measurements of samples of weight w. Once K_s is evaluated for a given sample, the minimum weight w required for a maximum relative standard deviation of R% can be readily calculated for a well-mixed sample.

To determine whether a homogenization method produces a well mixed material, sets of increments of varying weights are analyzed to obtain values for R, the relative subsampling, for each weight. A straight line is fit to R^2 (y-axis) vs. $1/w$ (x-axis). If the line passes through the origin (within experimental error), the material is considered to be well mixed.[14] Shaw collected, at random, sets of test portions weighing approximately 10, 20, 40 and 100 g in weight from a 5-kg laboratory sample of oil sand with a maximum particle size of 5 mm.[8] The results of his analyses, given in Table 2.1 indicate that the laboratory sample was well mixed in terms of bitumen because the origin fell within one standard deviation of the intercept but that it was not well mixed in terms of water and solids. When a sample is not well mixed (i.e. segregated), increasing the increment size by a factor x causes a reduction in sampling variance by a factor smaller than x so that the predictive capabilities of equation 2 are lost. The sampling variance associated with any increment size for a poorly mixed material can be determined by application of the general sampling theory of Visman. This method is described later in this chapter.

THE SAMPLING PLAN

Before sampling begins, the analyst should establish a model of the overall operation, which defines the population studied, the substance(s) measured, the extent to which speciation and distribution within the population are to be defined, and the precision required. The model should also identify all assumptions made about the population. Once the model is complete, a sampling plan can be established.

The plan should specify the size, number, and location of the sample increments, the extent of compositing, if applicable, and procedures for reduction of the gross sample to a laboratory sample to test portions. Before work begins, this should be written as a detailed protocol including procedures for all steps, from sampling through sample treatment, measurement, and data evaluation; if necessary, it should be revised as new information is obtained. The guidelines for data acquisition and quality evaluation set out by the ACS Subcommittee on Environmental Analytical Chemistry[9] are sufficiently general to be recommended for workers in all fields.

The protocol should spell out when, where, and how to take the sample increments and will establish, beforehand, on-site criteria for collection of a valid sample. Frequently, decisions about whether a component is foreign (not part of the population) must be made at the time of sampling. For example, extraneous material such as garbage found in a portion of oil sand being analyzed for bitumen might be considered foreign and, therefore, legitimately rejected. But should rocks be excluded? Rejection also becomes less clear with smaller items. If rocks are rejected should smaller stones also be rejected? How small? Criteria for such decisions should be established logically and systematically before sampling is initiated if possible.

The type of container, cleaning procedure, protection from contamination before and after sampling, refrigeration, and possible addition of preservatives should be specified. Plans calling for field blanks and/or field-spiked samples, because of the critical nature of the latter and the difficulties possible under field conditions, demand the utmost care to get meaningful results.

Whenever possible, the analyst should perform or directly supervise the sampling operation. Otherwise, he or she should provide a written protocol and make sure those collecting the samples are well trained so bias and contamination are minimized. No less important is careful labeling and recording of samples. A chain of custody to ensure the integrity of the samples from source to measurement is essential. Frequently, temperature, nature of the collecting device, atmospheric conditions, and so on must be recorded when the sample is taken. Omission or loss of such information may greatly decrease the value of a sample, or even render it worthless.

Sampling bulk materials. Once the substances to be determined and the precision desired have been specified, a sampling plan can be designed that considers:

- how many samples should be taken
- how large should each be
- from where in the bulk material (population) they should be taken
- whether individual samples should be analyzed or a composite prepared.

The relative homogeneity of the system affects sample size. Gross samples should be unbiased with respect to the different sizes and types of particles present in the bulk material. The size of the gross sample is often a compromise based on the heterogeneity of the bulk material on the one hand, and the cost on the other.

When the properties of a material to be sampled are unknown, a good approach is to collect a small number of samples, using experience and intuition as a guide to make them as representative of the population as possible, and analyze for the component of interest. From these preliminary analyses, the standard deviation s_s of the individual samples can be calculated, and confidence limits for the average composition established using

$$\mu = \bar{x} \pm ts_s/(n)^{1/2} \qquad (3)$$

where μ is the true mean value of the population, $\bar{x}$ is the average of the analytical measurements, and t is obtained from statistical tables for n measurements (often given as $n - 1$ degrees of freedom) at the desired level of confidence, usually 95%. Tables of t values are provided in books on quantitative analysis and statistics.[2-6]

On the basis of this preliminary information, a more refined sampling plan can be devised, as described in the following sections. After one or two cycles the parameters should be known with sufficient confidence to estimate the number of the samples with a specified level of confidence. Considerable savings in time and costs result from optimizing the sampling program.

Minimum number of individual increments. Unless the population is known to be homogeneous, or unless a representative sample is mandated by some analytical problem, sufficient replicate samples (increments) must be analyzed. The minimum number of sample increments necessary to achieve a given level of confidence can be estimated from

$$n = \frac{t^2 s_s^2}{R^2 \bar{x}^2} \times 10^4 \qquad (4)$$

where t is the Student's t-table value for the level of confidence desired, s_s and $\bar{x}$ are estimated from preliminary measurements on, or from previous knowledge of, the bulk material, and R is the percent relative standard deviation acceptable in the average. Initially t can be set at 1.96 for 95% confidence limits and a preliminary value of n calculated. The t value for this n can then be substituted and the system iterated to constant n. This expression applies if the sought-for component is distributed in a positive binomial, or a Gaussian distribution, characterized by having an average, μ, larger than the variance, σ_s^2. Remember that values of σ_s (and s_s) may depend greatly on the size of the individual samples.

Sometimes what is wanted is not an estimate of the mean but instead the two outer values or limits that contain nearly all of the population values. If we know the mean and standard deviation, then the intervals $\mu \pm 2\sigma$ and $\mu \pm 3\sigma$ contain 95% and 99.7% respectively, of all samples in the population. Ordinarily, the standard deviation σ is not known but only its estimate s, based on n observations. In this case we may calculate statistical tolerance limits of the form $\bar{x} \pm Ks$ with the factor K chosen so that we may expect the limits to include at least a fraction P of the samples with a stated degree of confidence.[7] Values for the factor K depend upon the probability of including the proportion P of the population, and the sample size, n. Note that this K is not the same as Ingamells's sampling constant K_s.

Sampling a segregated (stratified) material. Special care must be taken when assessing the average amount of a substance distributed throughout a bulk material in a nonrandom way. Such segregation may be found, for example, in oil sand, in different production batches in a plant, or in materials where settling is caused by differences in particle size or density. To obtain a valid sample of a material in which strata can be identified:[3]

- divide the material into real or imaginary segments (strata)
- further divide the major strata into real or imaginary subsections and select the required number of samples by chance (preferably with the aid of a table of random numbers)
- take samples proportional in number to the size of each stratum, if the major strata are not equal in size.

In general, it is better to use stratified random sampling rather than unrestricted random sampling, provided the number of strata is kept sufficiently small so that several samples can be taken from each stratum without increasing the standard deviation of the sampling step and so that possible variations within the parent population can be detected and assessed. Also, it is necessary to know the size of each stratum. This may be difficult to determine for bulk or field populations.

Minimum number and size of individual increments in segregated material. The Visman method. When a bulk material is highly segregated, or when the strata are not identifiable, a large number of samples must be taken from different segments. A useful guide to estimating the number of samples needed is given by Visman[10], who proposed that the variance in sample composition depends on the degree of homogeneity within a given sample increment and the degree of segregation between sample increments.

$$s_s^2 = A/wn + B/n \qquad (5)$$

where s_s^2 is the variance of the average of n samples, each having a weight w and A and B are constants for a given bulk material. A is called a homogeneity constant, and B a segregation constant.

The simplest means of estimating A and B entails analysis of two sets of increments of widely varying weights w_{Lg} and w_{Sm}. The two extreme weights used in the test for segregation described in the section on subsampling, will suffice if $w_{Lg} \geq 10\ w_{Sm}$. Sampling uncertainties for each set, s_{Lg} and s_{Sm} are used to determine the constants by:

$$A = \frac{w'_{\mathrm{Lg}} w'_{\mathrm{Sg}}}{w'_{\mathrm{Lg}} - w'_{\mathrm{Sm}}} (s_{\mathrm{Sm}}{}^2 - s_{\mathrm{Lg}}{}^2) \quad \text{and} \tag{6}$$

$$B = s_{\mathrm{Lg}}{}^2 - \frac{A}{w'_{\mathrm{Lg}}} \tag{7}$$

For multi-tonne stockpiles of mined Athabasca oil sand, *A* and *B* have approximate values of 100 g%^{2} and 0.8%^{2} respectively for determination of bitumen content.[15]

The optimum increment weight *A*/*B* is the weight of a single increment which should be collected if the segregation and random distributions are to contribute equally to the sampling variance. Sampling variance changes significantly with increment weight below 10 *A*/*B*, but above that limit, little sampling precision is gained or lost by changing the weight of increments collected.

Sampling materials in discrete units. If the lot of material under study occurs in discrete units, such as truckloads, drums, bottles, tank cars, or the like, the variance of the analytical result is the sum of the variance between units in the lot, the average variance of sets of samples taken from within one unit, and the variance of the analytical operations. The contribution from each depends upon the number of units in the lot and the number of samples taken:[1]

$$\sigma_x{}^2 = \frac{\sigma_b{}^2}{n_b} \frac{(N - n_b)}{N} + \frac{\sigma_w{}^2}{n_b n_w} + \frac{\sigma_t{}^2}{n_t} \tag{8}$$

where $\sigma_x{}^2$ = variance of the mean, $\sigma_b{}^2$ = variance of the units in the lot, $\sigma_w{}^2$ = average variance of the samples taken from a unit, $\sigma_t{}^2$ = variance of the analytical operations; N = number of units in the lot; n_b = number of randomly selected units sampled; n_w = number of randomly drawn samples from each unit selected for sampling; and n_t = total number of analyses, including replicates, run on all samples.

If stratification is known to be absent, preparing a composite sample saves measurement time and effort. Equation 3 applies to this situation also. If the units vary significantly in weight or volume, the results should be weighted accordingly.

For homogeneous materials, including some liquids and most gases, $\sigma_w{}^2$ is zero, and the second term on the right side of Equation 8 drops out. If all units are sampled, $n_b = N$ and the first term on the right of Equation 8 also drops out.

CONCLUDING COMMENTS

Sampling is not simple. It is most important in the worst situations. When $\bar{x}$, s, K_s, A, and B are known exactly, it is easy to calculate the statistical sampling uncertainty and to determine the number and size of the samples needed for a given precision. If these quantities are known only approximately, or perhaps not at all, then preliminary samples and measurements must be taken, and from these, more precise sampling procedures developed. Ultimately a sampling plan that optimizes the quality of the results while holding down time and costs can be achieved.

Sampling theory cannot replace experience and common sense. Used in concert with these qualities, however, it can yield the most information about the population being sampled with the least cost and effort. All analytical chemists, even though they may possess special expertise in a particular separation or measurement technique, should know enough sampling theory to ask intelligent questions about the samples provided, to take subsamples without introducing additional uncertainty and, if necessary, to plan and perform uncomplicated sampling operations.

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Chapter 3: CARBON AND HYDROGEN

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CARBON AND HYDROGEN

DEFINITION

Carbon and hydrogen are the two major elements found in bitumen, heavy oil and their upgraded products.

SIGNIFICANCE

The ratio of hydrogen to carbon is a measure of the quality of a crude. From this ratio, the amount of hydrogen that will be required to upgrade the crude can be estimated. A light (higher value) crude has a higher H/C ratio than a heavy (low value) crude.

The levels of carbon and hydrogen, when combined with NMR and average molecular weight data, are also used to deduce average molecular structures.

METHODS

1. ASTM D3178: Carbon and Hydrogen in the Analysis Sample of Coal and Coke

1.1 Application

This method was designed for the simultaneous determination of carbon and hydrogen in coal and coke, and is also used for measuring these elements in bitumen and heavy oil.

1.2 Summary of the Method

A 0.2-g test sample is burned in a combustion tube packed with cupric oxide and lead chromate or silver. These inorganic compounds aid combustion and remove interfering substances such as oxides of sulfur. The carbon dioxide and water produced during combustion are adsorbed on pre-weighed ascarite and anhydrous magnesium perchlorate, whose increases in weights are measures of the weight percentage of carbon and hydrogen in the sample. Although nitrogen in excess of 2% in the test sample can lead to high results for carbon due to adsorption of nitrogen oxides, the level of nitrogen in bitumen is not high enough to warrant the use of nitrogen oxide scrubbers.

1.3 Precision

	Repeatability (%)	**Reproducibility (%)**
Carbon		
ASTM D3178	0.3	-
Phillips[a]	1.5	2.7
Smith[b]	0.3	-
Hydrogen		
ASTM D3178	0.07	-
Phillips[a]	0.6	1.1
Smith[b]	0.2	-

[a] Precision was estimated from duplicate analyses by four laboratories of a California heavy oil blend containing 83.4% carbon and 11.5% hydrogen and a Maya crude containing 84.0% carbon and 11.3% hydrogen. One laboratory used a home-made apparatus, a second used a Coleman analyzer, a third a CBC Micro-Pregl apparatus and a fourth followed ASTM D3178.[11]

[b] From the data in Table 3.4.

2. Automated Elemental (C, H, N) Determinations

2.1 Applications

This technique permits simultaneous determination of carbon, hydrogen and nitrogen in a variety of materials including bitumen and heavy oil.

2.2 Summary of the Methods

A 0.5- to 5-mg test sample is burned over a catalyst in a stream of oxygen to produce carbon dioxide, water and nitrogen oxides. In the LECO CHN-600 analyzer, the nitrogen oxides are reduced to elemental nitrogen over copper. Carbon dioxide and water are measured in an aliquot of the combustion products by infrared detectors, and the sample signal compared to the signals from standard samples or from dosing with known quantities of the pure gases.

The Perkin-Elmer 240C Elemental Analyzer employs three pairs of thermal conductivity cells in series. The combustion gases are swept with helium through the cells. Between the first pair of cells, a magnesium perchlorate trap adsorbs the water from the gas mixture, and the signal obtained from the bridge circuit between the two cells is a measure of the amount of water removed from the mixture. Carbon dioxide is adsorbed on a strong caustic support between the second pair of cells and a signal is generated which is proportional to the amount of gas removed. The nitrogen in the remaining gas sample is measured by comparing the thermal conductivity of the sample with that of pure helium. The signals for the sample are compared to those from a standard such as acetanilide.

In the Carlo Erba Analyzer, the combustion gases are separated on a Porapak QS (80-100 mesh) column, a vinyl-ethylbenzene-divinylbenzene polymer, and detected by thermal conductivity. The signals are compared to those from a standard.

Measurement of nitrogen will be described in detail in Chapter 4.

2.3 Precision

	Repeatability (%)	Reproducibility (%)
Carbon		
ACOSA[a]	0.7	1.7
Phillips[b]	1.0	1.7
Smith[c]	0.4	-
Wallace[d]	0.8 (Athabasca)	-
	1.0 (Asphalt Ridge)	
Mahlow[e]	0.6	-
Hydrogen		
ACOSA[a]	0.6	0.7
Phillips[b]	0.3	0.3
Smith[c]	0.2	
Wallace[d]	0.4 (Athabasca)	
	0.4 (Asphalt Ridge)	
Mahlow[e]	0.1	

[a] Seven laboratories conducted triplicate analyses of an Athabasca bitumen (83.0% carbon, 10.5% hydrogen) and a Lloydminster heavy oil (83.3% carbon, 11.0% hydrogen).

[b] Five laboratories conducted duplicate analyses of the California heavy oil blend and the Maya crude samples described in section 1.3.[11]

[c] From the data in Table 3.4.

[d] Eight pairs of Athabasca bitumen and of Asphalt Ridge bitumen samples were prepared under a variety of solvent extraction conditions. Repeatability was based on the pooled standard deviations from each pair and therefore contains an element of uncertainty due to sample preparation. The data were corrected for residual solvent and solids.[15]

[e] From the data in Table 3.1.

DISCUSSION

Development of Elemental Analyzers

Carbon and hydrogen determinations have historically been based on pyrolysis and oxidation of a test sample to form carbon dioxide and water which are measured gravimetrically or by thermal conductivity. One method, however, entails conversion of the water produced during combustion to acetylene by reaction with calcium carbide.[9] This method was not used in the ACOSA or the Phillips sample exchanges.

Errors in combustion-gravimetric methods (Pregl) generally arise from the adsorption of gases and weighing of the adsorption tubes rather than the combustion step. Francis reviewed the problems arising from the use of different styles of adsorption tubes.[5] He found that a major source of error could be attributed to fluctuations in the temperatures of the tubes, leading to weighing errors. Simon and co-workers reported that the Pregl method could not be applied to samples weighing less than 1 mg and that the method must be used by skilled, well-trained analysts having considerable experience and patience.[13] Their listing of potential automated methods, though prepared in 1962, is still complete.

The operation of automated carbon-hydrogen-nitrogen analyzers has been described by Ma and Rittner[7] (Carlo-Erba), as well as Condon[3] and Culmo[4] (Perkin-Elmer). Operating manuals for these analyzers describe procedures for identifying leaks, incomplete combustion, contamination of the carrier and pyrolysis gases, and exhaustion of scrubbers and adsorbers. A significant systematic error in automated elemental analysis can occur if precautions are not taken to prevent the loss of low-boiling-point components prior to injection of the sample into the combustion zone. The use of tin or indium capsules, which can be sealed, is required for analysis of volatile materials such as naphthas and kerosenes. There is a preference to use open boats for bitumens and heavy oils. However, during evacuation of the analyzer prior to combustion, a significant portion of the sample may be lost. Mahlow at the University of Alberta cools the glass tube holding the boat with dry ice to minimize the loss of light ends from heavy samples.[8] For Lloydminster

Table 3.1: Comparison of Carbon and Hydrogen Data With and Without Cooling of the Injection Tube[8]

	Carbon (%)		Hydrogen (%)	
	Cooled	Not cooled	Cooled	Not cooled
Suncor coker feed bitumen				
A	83.66	83.39	10.55	10.47
B	84.34	83.06	10.59	10.39
C	84.00	82.99	10.55	10.46
D	83.98	83.47	10.50	10.37
E	83.99	83.47	10.54	10.51
$\bar{x}$	83.99	83.28	10.55	10.44
s	0.24	0.23	0.03	0.06
Lloydminster heavy oil				
A	84.20	83.44	11.00	10.90
B	84.43	83.92	11.06	11.00
C	84.17	83.33	11.12	10.97
D	83.97	82.93	11.02	10.86
E	84.50	82.54	11.11	10.85
$\bar{x}$	84.25	83.23	11.06	10.92
s	0.21	0.52	0.05	0.07

Table 3.2: Parameters Affecting Precision on the Perkin-Elmer 240 Analyzer[12]

Source	Range	Variation	Error
Weighing	1 mg	1 μg	0.1%
Readout	25 mV	25 μV[a]	0.1%
Detector voltage	18 V	<5 mV	<0.03%
Pressure	1500 mm Hg	<1 mm Hg	<0.06%
Temperature	70°C	<0.05°C	<0.07%

[a] With scale expansion.

heavy oil, errors of 1% relative in both carbon and hydrogen occur if this precaution is not taken (Table 3.1). The loss of light components prior to carbon and hydrogen measurements could cause errors of 100% relative in estimates of oxygen content if that element is determined by difference.

At an International Symposium on Microchemical Techniques, Perkin-Elmer presented evaluations of their Model 240 elemental analyzer in which produced gases are detected by TCDs.[12] They outlined parameters affecting precision. According to their figures the standard deviation of weighing the sample and obtaining a readout are much larger than the uncertainty arising from detector fluctuations. The errors listed in Table 3.2 indicate the repeatability of this type of analysis, discounting incomplete combustion, leaks, etc., would be

$2.83 \times (0.1^2+0.1^2+0.03^2+0.06^2+0.07^2)^{1/2} = 0.5\%$ relative.

The repeatability statements for percent carbon in section 2.3 agree well with this estimate, but repeatability of up to 6% relative was reported for hydrogen.

Smith, Meyers and Shaner compared data from the analysis of typical petroleums by using a PE-240 CHN analyzer with classical Dumas determinations.[14] Their classical data included in Table 3.3 had a reproducibility of 6.5% for carbon and 1.1% for hydrogen. The percent carbon reproducibility for the classical methods was more than double that found in the Phillips cooperative study and the percent hydrogen reproducibility was the same. Further analyses of a Baja crude exhibited much better agreement between the classical and Perkin-Elmer data (Table 3.4). In the ACOSA and Phillips cooperative studies, the mean results from elemental analyzers did not differ significantly from the combustion-gravimetry data at the 95% level of confidence (Table 3.5).

Infrared detection of carbon dioxide and water is a recent development in automated analysis. It was first

Table 3.3: Comparison of Carbon and Hydrogen Data for Typical Petroleum Samples Using Combustion-Gravimetry and a Perkin-Elmer Analyzer (Reprinted with permission from Mikrochim. Acta [Wien] 1972, 217-222.)

	Classical lab 1		Classical lab 2		PE-240 C-H-N	
	Carbon (%)	Hydrogen (%)	Carbon (%)	Hydrogen (%)	Carbon (%)	Hydrogen (%)
Distilled oil	89.77	6.51	89.39	6.71	90.33	7.04
Anthracene oil	90.88	6.11	90.88	5.55	91.47	5.83
Hydrogenated coal	91.32	7.34	91.76	7.20	91.83	7.44
Asphaltenes from Taggert coal	89.64	6.26	83.89	6.88	89.66	5.33
Asphalt hydrogenated	85.35	10.45	85.57	10.74	85.92	10.39
Lagomed resid hydrogenated	87.41	11.90	83.44	12.85	87.39	11.87
Lagomedio resid hydrogenated	86.66	12.29	86.42	12.67	86.24	11.88
Lagomedio resid	86.08	12.86	86.42	12.84	87.70	12.09
Hydrocracked oil	82.09	11.30	88.19	10.94	86.94	11.19
Hydrocracked oil	83.88	10.95	88.16	11.87	88.02	12.09

Table 3.4: Determination of Carbon and Hydrogen in Baja Crude (Reprinted with permission from Mikrochim. Acta [Wien] 1972, 217-222).

Classical		PE-240	
Carbon (%)	Hydrogen (%)	Carbon (%)	Hydrogen (%)
84.45	11.42	84.99	11.79
84.72	11.61	84.68	11.68
84.69	11.55	84.94	11.88
84.65	11.60	84.72	11.77
84.61	11.54	84.79	11.69

described by Allain and Le Francois and is now employed in the LECO analyzer. The IR detectors are described by Allain and Francois as being more reliable than thermal conductivity detectors.[1] Repeatability for a variety of petroleum samples is provided in Table 3.6.

The LECO analyzer also permits analysis of samples weighing up to 200 mg, a factor on the order of 40 greater than the other analyzers. Increasing test sample size to 200 mg to obtain a more representative mix of bitumen and solids and a more precise estimate of carbon and hydrogen, however, does not give the benefits one would expect. The Visman sampling constants $A = 0.12\ \text{mg}\%^2$ and $B = 0\%^2$ derived in Chapter 13 describing ash determinations can be used to estimate that for an Athabasca bitumen containing 0.5% solids, an increase in test sample size from 5 to 200 mg would decrease the variability in solids between ash samples from 0.15 to 0.02%.[3]

In the ACOSA cooperative study, the standard deviation of the carbon determination using elemental analyzers was 0.25% for an Athabasca bitumen containing 83.0% carbon and 0.5% solids. An analysis of the propagation of errors shows that if the labs used a test sample of 5 mg, the standard deviation in carbon determinations for a pure bitumen, containing no solids and therefore no variability due to solids, would have been 0.21% because

$$\%\ C_{\text{pure bitumen}}\ (x) \times (1 - \text{wt. fraction of ash } (y)) = \%\ C_{\text{bitumen plus solids}}\ (z) \tag{1}$$

or

$$z = x\ (1 - y) \tag{2}$$

$$\Delta z = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta(1-y)}{1-y}\right)^2}\ |z| \tag{3}$$

$$0.25 = \sqrt{\left(\frac{\Delta x}{83.0}\right)^2 + \left(\frac{.0015}{.995}\right)^2} \times 83.0$$

$$\Delta x = 0.21$$

Table 3.6: Determination of Carbon and Hydrogen in Petroleum Products with IR Detection of Combustion Gases (Reprinted with permission from Mikrochim. Acta [Wien] 1982I, 97-103.)

Compounds	Mean (%)	Standard deviation (%)	Repeatability (%)
Carbon			
Bright stock solvent	86.1	0.3	0.9
Heavy fuel	84.4	0.2	0.7
Vacuum residue	83.7	0.2	0.8
Hydrogen			
Bright stock solvent	13.00	0.06	0.18
Heavy fuel	10.46	0.08	0.26
Vacuum residue	10.43	0.06	0.18
C/H			
Bright stock solvent	6.61	0.04	0.14
Heavy fuel	8.06	0.06	0.20
Vacuum residue	8.02	0.04	0.14

Table 3.5: Comparison of Carbon and Hydrogen Data from Cooperative Studies[a]

	Carbon (%)		Hydrogen (%)	
	Elemental analyzer	Combustion-gravimetry	Elemental analyzer	Combustion-gravimetry
ACOSA				
Athabasca bitumen	82.88	83.22	10.49	10.44
Lloydminster heavy oil	83.11	83.60	10.98	10.94
Phillips[11]				
California heavy oil	84.16	83.26	11.43	11.63
Maya crude	83.69	83.43	11.35	11.39

[a] In both cooperative studies, four laboratories reported combustion-gravimetry data and eight laboratories used automated elemental analyzers.

For an analyzer using a 200-mg test sample and giving an analytical uncertainty for pure bitumen, Δx, of 0.21

$$\Delta z = \sqrt{\left(\frac{0.21}{8.30}\right)^2 + \left(\frac{.0002}{.995}\right)^2} \times 83.0$$
$$= 0.21$$

It is concluded therefore, that solids variability at the 5-mg test sample size contributes only slightly to the overall uncertainty in an analysis and the use of a 200-mg test sample for percent carbon determinations totally eliminates the effect of solids variability. Using the same set of calculations but with Δx equalling 0.21 and x equalling 10.5, it can be shown that the effect of solids on analytical uncertainty for hydrogen is also insignificant. Therefore, the large test portion required by the LECO analyzer does not lead to the same reductions in sampling uncertainty for bitumen as it would for say, coal, which sometimes contains high levels of solids. At the molecular level, it is difficult to conceive that carbon and hydrogen would vary significantly in a 5-mg sample which contains approximately 6×10^{18} molecules.

On the other hand, Glass and Cowell did perceive that analysis conducted on a larger scale would be more accurate and precise.[6] They did not state whether their concern related to obtaining representative samples or to the ease of sample handling and reduction in instrumental errors. They vaporized and pyrolyzed 500-mg samples in nitrogen and oxidized the products to carbon dioxide and water over copper oxide at 800°C. The water was adsorbed on magnesium perchlorate. Nitrogen was used to permit better control of the combustion. Oxygen was introduced into the combustion chamber later to oxidize the residue and regenerate the copper oxide. A repeatability of 0.06% was found for hydrogen from the duplicate analysis of 500-mg test samples of various petroleum products listed in Table 3.7. The accuracy of the method was verified by analysis of standard compounds as described in Table 3.8.

Oita and Babcock[10] automated the combustion part of the Glass and Cowell method and added an Ascarite adsorber to trap the carbon dioxide. Their estimates of repeatability for carbon and hydrogen were 0.09% and 0.07% based on the data in Table 3.9. They too confirmed the accuracy of the method by analysis of standard samples (Table 3.10).

Gravimetric methods preclude the systematic error which can occur in thermal conductivity measurements of gas mixtures if the standard and sample are not closely matched. This error rarely exceeds 0.2% in a carbon determination and can generally be ignored. Clerc and Simon provide a thorough discussion of this topic.[2]

The presence of water in a test sample causes a decrease in the measured carbon but no change in the measured hydrogen content. For example, analysis of a crude oil with 84.00% carbon and 11.00% hydrogen containing 1% water would yield reported values (disregarding random error) of 83.16% carbon and 11.00% hydrogen. Water does not cause a significant error in the hydrogen value because its hydrogen content and that of bitumen are so similar, but a 1% water content changes the measured H/C atomic ratio from 1.57 to 1.59 because of its effect on the measured level of carbon.

Results of Interlaboratory Studies

The most significant result of the ACOSA and Phillips studies was the failure of the participating laboratories to approach the precision reported in ASTM D3178 or by the developers of the instruments used. Furthermore, the errors in the absolute values for carbon and hydrogen did not follow any trends.

Figures 3.1 and 3.2 are two-sample plots of the H/C atomic ratios for the samples analyzed in the studies.

Table 3.7: Determination of Hydrogen in Nonvolatile Petroleum-Based Materials (Reprinted with permission from Anal. Chem. 1971, 43, 678-681. Copyright 1971, American Chemical Society.)

Sample Number	Description	Hydrogen (%)
1	Waxy product	13.67
		13.72
2	Waxy product	12.71
		12.69
3	Waxy product	12.82
		12.80
4	Waxy product	12.82
		12.77
5	Liquid product	13.77
		13.77
6	Liquid product	13.63
		13.55
7	Liquid product	13.19
		13.21
8	Residuum	10.36
		10.37
9	Waxy product	11.98
		11.97
10	Residuum	10.39
		10.40
11	Liquid product	11.69
		11.71
12	Liquid product	13.29
		13.25

$s_{pooled} = 0.02$ Repeatability $= 2.83 \times 0.02 = 0.06$

Table 3.8: Determination of Hydrogen in Known Compounds (Reprinted with permission from Anal. Chem. 1971, 43, 678-681. Copyright 1971, American Chemical Society.)

		Hydrogen (%)		
	Source[a]	Actual	Found	Deviation
Benzoic acid	NBS	4.95	4.94	−0.01
			4.94	−0.01
			4.94	−0.01
Phenanthrene	MC&B	5.66	5.67	+0.01
			5.69	+0.03
Triphenylmethanol	DPI	6.19	6.20	+0.01
			6.21	+0.02
Hexatriacontane	DPI	14.71	14.66	−0.05
			14.65	−0.06
Hexadecane	H-W	15.13	15.10	−0.03
			15.08	−0.05
			15.12	−0.01
			15.11	−0.02
			15.18	+0.05
Dodecane	PPC	15.38	15.39	+0.01
			15.36	−0.02
			15.35	−0.03
			15.39	+0.01
Decalin	DPI-SiO^2	13.12	13.08	−0.04
			13.09	−0.03
Hexadecane-dibenzo-thiophene blend	H-W/DPI	14.60	14.59	+0.02
			14.62	+0.02
			14.62	

[a] NBS:	National Bureau of Standards	H-W:	Humphrey-Wilkinson
MC&B:	Matheson, Coleman and Bell	PPC:	Phillips Petroleum Company, Pure Grade
DPI:	Distillation Products Industries	DPI-SiO$_2$:	Distillation Products Industries, silica gel percolated

Table 3.9: Determination of Carbon and Hydrogen in Pipe Still Resid (Reprinted with permission from Anal. Chem. 1980, 52, 1007-1008. Copyright 1980, American Chemical Society.)

Run No.	Carbon (%)	Hydrogen (%)
1	84.81	11.08
2	84.79	11.06
3	84.83	11.10
4	84.85	11.11
5	84.84	11.08
6	84.82	11.08
7	84.81	11.08
8	84.81	11.09
9	84.85	11.08
10	84.78	11.04
11	84.82	11.13
$\bar{x}$	84.82	11.08
s	0.032	0.024
Repeatability	0.09	0.07

Table 3.10: Determination of Carbon and Hydrogen in Known Compounds (Reprinted with permission from Anal. Chem. 1980, 52, 1007-1008. Copyright 1980, American Chemical Society.)

	Carbon (%)		Hydrogen (%)	
Compound	Actual	Measured	Actual	Measured
Benzoic acid	68.86	68.86	4.95	4.96
Acetanilide	71.09	71.09	6.71	6.73
Toluene	91.25	91.25	8.75	8.77

In the ACOSA cooperative study, (Figure 3.1) there was a tendency for a laboratory that reported a high H/C ratio for Athabasca bitumen to also report a high H/C ratio for the Lloydminster sample. The H/C atomic ratios for the twelve laboratories in the Phillips study are plotted in Figure 3.2. When the three points which are widely scattered from the bulk of the data are ignored, the same trend as in Figure 3.1 is apparent. This type of trend is symptomatic of calibration errors, use of exhausted or nearly-exhausted adsorbers, and leaks in the system between the hydrogen and carbon detectors.

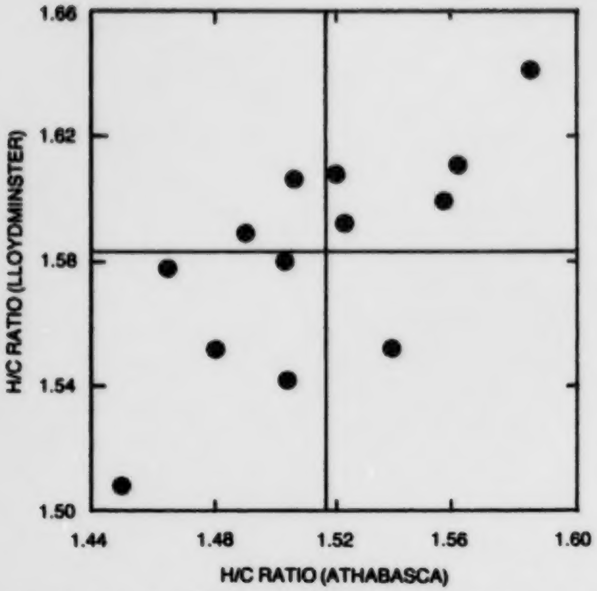

Figure 3.1: Comparison of H/C Atomic Ratios as Determined by Labs in the ACOSA Study

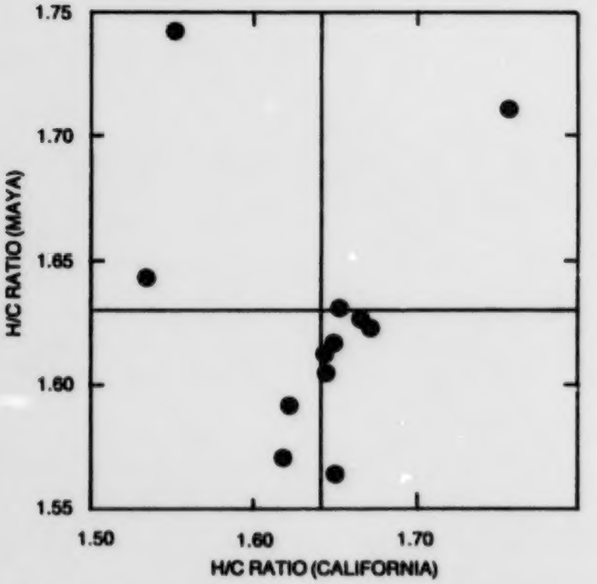

Figure 3.2: Comparison of H/C Atomic Ratios as Determined by Labs in the Phillips Study

It is unlikely that the variations in H/C ratio are due to errors in the original weighing of the sample or inclusion of fine solid particles in some of the test portions, as these errors would affect the absolute carbon and hydrogen values rather than the ratios. As the average water contents of the crudes in the Phillips study were in the range of 0.5%, it is feasible that the distribution of water droplets if they were large enough, throughout 1-mg test portions, would be sufficiently variable to cause measurable errors in the H/C ratio. Incomplete combustion also tends to affect the carbon more than the hydrogen results because the char is carbon-rich.

SUMMARY

The principles behind carbon and hydrogen determinations have remained relatively unchanged from manual to automated methods. Despite the acceptance of the Pregl combustion, the precision in recent studies of bitumen analysis has been much poorer than anticipated. However, some of the uncertainty may be attributable to entrained water in the small test portions rather than to faulty analyses.

Some researchers have reverted to gravimetric determinations as elemental analyzers have not delivered the required precision and accuracy due either to the small size of the test portions or uncertainty in the measurement of combustion gases. At the same time, the researchers recommend the use of more controlled combustion conditions by using nitrogen in place of oxygen. This modification has not been widely adopted since the data quality required does not generally justify the extra effort.

On average, classical combustion gravimetry methods and the more recent automated elemental analyzers provide equivalent carbon and hydrogen data. Sample variability at the 5-mg test sample size does not appear to be a significant source of random error for heavy crudes.

An analyst should be prepared to incorporate corrections for solids and water to obtain accurate data. Solids affect the carbon and hydrogen values equally while the presence of water has little impact on the measured hydrogen content.

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Chapter 4: NITROGEN

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NITROGEN

DEFINITION

Nitrogen is a naturally occurring element found in bitumens and heavy oils.

SIGNIFICANCE

Organic nitrogen compounds in petroleum feedstocks cause serious problems during upgrading, especially when the nitrogen level exceeds 0.5%. The basicity of most nitrogen compounds causes poisoning of acidic and metal-containing catalysts in the cracking process.[4] Nitrogen compounds are difficult to remove by hydrogenation so their presence determines the severity and cost of the process.[19]

METHODS

1. UOP 653-73: Total Nitrogen in Organic Compounds by Micro Dumas Gas Chromatography

1.1 Application

This method is used to determine levels of nitrogen above 0.01%.

1.2 Summary of the Method

The conditions of the test may vary for different elemental analyzers. The test sample is usually burned at 800 to 1000°C over a catalyst such as chromium oxide or cupric oxide to produce nitrogen oxides. These are reduced to nitrogen gas over copper at 500 to 600°C and the nitrogen is separated from the combustion gases on a gas chromatographic column. In Perkin-Elmer, Leco and Carlo Erba analyzers, the nitrogen is measured by a thermal conductivity detector.

In one nitrogen-specific analyzer (the Micro-Rapid-N), the nitrogen is isolated and measured by volume in a buret.[3]

1.3 Precision

	Repeatability (%)	**Reproducibility (%)**
UOP[a]	0.002	-
ACOSA[b]	0.09	0.26
Phillips[c]	0.07	0.22
Wallace[d]	0.10	-

[a] For a vacuum gas oil containing 0.25% N.

[b] From triplicate analyses by five laboratories of an Athabasca bitumen containing 0.4% nitrogen and a Lloydminster heavy oil containing 0.3% nitrogen.

[c] From duplicate analyses by six laboratories of a California heavy oil containing 0.6% nitrogen and a Maya crude containing 0.4% nitrogen.[13]

[d] From the analysis of eight pairs of samples of Athabasca bitumen with approximately 0.5% nitrogen and Asphalt Ridge bitumen with approximately 1.2% nitrogen. The members of each pair were extracted under identical conditions. Therefore, this estimate of repeatability includes some contribution from sample preparation. Nitrogen values were corrected for solids and residual solvent.

2. ASTM D3228: Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method and UOP Method 384-76: Nitrogen in Petroleum Distillates and Heavy Oils by Acid Extraction or Direct Kjeldahl Procedure

2.1 Application

ASTM D3228 is used to determine nitrogen at levels up to 2% in bitumen and heavy oil. The Kjeldahl methods may not be suitable for analyzing materials containing N-O and N-N linkages. These types of compounds are converted to either elemental nitrogen or nitrogen oxides which are not detected.

2.2 Summary of the Method

A test sample, whose size depends on the size of the apparatus, is digested in a mixture of concentrated sulfuric acid, potassium sulfate, mercuric oxide and copper sulfate. The nitrogen is converted to ammonia, which is distilled into a boric acid solution and titrated with standard sulfuric acid using methyl purple as an indicator.

UOP 384-76 also describes an acid extraction procedure which concentrates the nitrogen in samples containing 0.1 to 100 mg/kg of nitrogen. The extraction is not usually required when analyzing heavy crudes which contain higher levels of nitrogen.

2.3 Precision

	Repeatability (%)	**Reproducibility (%)**
ASTM D3228[a]	$0.066 \sqrt{\%N}$	$0.190 \sqrt{\%N}$
ACOSA[b]	0.02	0.05
Phillips[c]	0.04	0.04
Lake[d]	0.05	-

[a] These values correspond to repeatability and reproducibility of 0.04 and 0.12% for a "typical" crude containing 0.4% nitrogen.

[b] From triplicate analyses conducted by four laboratories of the Athabasca bitumen and Lloydminster heavy oil samples described in section 1.3.

[c] From duplicate analyses by three laboratories of the California heavy oil and Maya crude samples described in section 1.3.[15]

[d] From duplicate analyses of six shale oil and four petroleum samples with nitrogen contents ranging from 0.014 to 10.22%.[11]

3. Syncrude Analytical Method 5.10: Determination of Nitrogen in Liquid Petroleum Hydrocarbons by Chemiluminescence

3.1 Application

This method is used to determine the level of chemically bound nitrogen in liquid hydrocarbons by conversion to nitrogen dioxide. Azo compounds (N-N linkages) tend to convert to nitrogen gas and yield low levels of nitrogen dioxide on combustion.

3.2 Summary of the Method

A sample of bitumen is diluted with toluene to produce a solution with an expected nitrogen content of 50 to 100 nanograms per litre. The solution is injected by syringe into the analyzer where it is pyrolyzed over cupric oxide in an oxygen-rich atmosphere at 900 to 1100°C. Nitrogen oxide produced during pyrolysis reacts with ozone in a reaction chamber to form excited nitrogen dioxide (NO_2^*):

$$NO + O \rightarrow NO_2^* + O_2$$

As the excited nitrogen dioxide reverts to the ground state, photoemission occurs. The level of photoemission from the sample is compared to that from a standard such as carbazole.

The syringe injection system in the Dohrmann analyzer can be replaced by a boat inlet system to allow analysis of solid or semi-solid samples such as bitumen.

3.3 Precision

	Repeatability (%)	**Reproducibility (%)**
ACOSA[a]	0.01	0.14
Phillips[b]	0.02	0.09
Dolle[c]	0.02	-

[a] From triplicate analyses by three laboratories of the Athabasca bitumen and Lloydminster heavy oil samples described in section 1.3.

[b] From duplicate analyses by four laboratories of the California heavy oil and Maya crude samples described in section 1.3.

[c] As many as six replicates from a variety of petroleum products and crude oils containing from 0.1 to 0.3% nitrogen were analyzed.[5]

4. ASTM D3431: Trace Nitrogen in Liquid Petroleum Hydrocarbons (Microcoulometric Method)

4.1 Application

This method covers the determination of total nitrogen within the range 2 to 5000 mg/kg in liquid hydrocarbons boiling between 50 and 500°C. Modifications to this technique have been proposed that may permit analysis of heavier materials.[23]

4.2 Summary of the Method

The test sample, diluted in an appropriate solvent or introduced in a boat, is pyrolyzed in a stream of hydrogen over a nickel catalyst at approximately 800°C so that the nitrogen is converted to ammonia. The ammonia is swept into a titration vessel where it is converted to ammonium hydroxide by the reaction:

$$NH_3 + H_2O \rightarrow NH_4OH.$$

The ammonium hydroxide is titrated by H^+ in solution by:

$$NH_4OH + H^+ \rightarrow NH_4^+ + H_2O.$$

The amount of current required to regenerate H^+ from H_2 at the generator to return the solution to its original pH is recorded and used to calculate the amount of NH_3 entering the titration cell.

4.3 Precision

ASTM precision statements cover materials with a final boiling point of 550°C and so are not applicable to heavy crudes.

No participants in either the ACOSA or Phillips interlaboratory studies used the microcoulometric method for measuring nitrogen.

5. Neutron Activation Analysis (NAA)[7]

5.1 Application

Neutron activation analysis is used to measure nitrogen at levels above 0.05% in fossil fuels.

5.2 Summary of the Method

A test sample is exposed to 14-MeV neutrons produced by the $^3H(d,n)^4He$ reaction in a neutron generator. These neutrons induce the $^{14}N(n, 2n)^{13}N$ nuclear reaction. The ^{13}N radionuclide decays by positron (positively charged electron) emission with a 9.96-minute half-life. The positron combines with an electron to produce 0.511-MeV annihilation radiation which is detected by NaI(Tl) detectors. The level of annihilation radiation for the sample is compared to that for a standard.

5.3 Precision

The number of determinations used for precision calculations for each sample is given in brackets.

Sample description	Nitrogen (%)	Repeatability (%)
Residual fuel oil	0.039	0.052 (6)
Residual fuel oil	0.111	0.030 (4)
Residual fuel oil	0.286	0.082 (4)
Coal liquefaction ASOH	0.699	0.042 (4)
Coal liquefaction ASB	0.626	0.147 (5)
Coal liquefaction VSOH	0.879	0.089 (4)
Coal liquefaction VSB	2.26	0.45 (4)
Shale oil	2.00	0.16 (4)
Petroleum residuum	0.211	0.026 (5)

ASOH = atmospheric still overhead
VSOH = vacuum still overhead
ASB = atmospheric still bottoms
VSB = vacuum still bottoms

DISCUSSION

Development of the Kjeldahl Method and Comparison with Other Analytical Methods

The Kjeldahl method for measuring nitrogen was developed for the measurement of protein nitrogen in 1883. In the original method the sample was digested in sulfuric acid to produce ammonia which was distilled into boric acid and titrated. Wilfarth recommended the use of mercury as an oxidation catalyst to decompose the sample (1885)[22] and Gunning proposed the addition of potassium sulfate to raise the digestion temperature so that fewer compounds would be refractory under conditions of decomposition (1899).[8] The Kjeldahl-Wilfarth-Gunning method is the basis for ASTM D3228 and UOP 384-76 which are used for analysis of petroleum products.

The effect of varying digestion conditions in the Kjeldahl analysis was the subject of almost 150 papers which were reviewed by Bradstreet in 1940.[2] Kirk's review in 1950 provided a concise explanation of the reactions that take place in a Kjeldahl digestion.[9] To summarize, during digestion an oxidizer is necessary to convert the carbon and hydrogen in the test sample to CO_2 and H_2O but at the same time, conditions must be favorable for the reduction of nitrogen to ammonia. Strong oxidants such as selenium or copper oxides can cause production of nitrogen or nitrogen oxides which are not detected.

Low digestion temperatures caused by too little potassium sulfate result in excessive digestion times and even incomplete digestion of the sample, while high digestion temperatures caused by an excess of potassium sulfate result in oxidation of ammonia. No single set of conditions is suitable for all materials.

Lake and co-workers decided that, of the compounds likely to be found in shale oil and petroleum, pyridine was the most refractory.[11] They prepared a solution of pyridine in a hydrocarbon solvent and measured the recovery of nitrogen at various digestion temperatures, controlled by the K_2SO_4:H_2SO_4 ratio for digestion times ranging from one to three hours. Their results, summarized in Figure 4.1, show that a minimum temperature of 370°C is required for complete recovery of nitrogen. They also determined the levels of nitrogen in tar bases and ammonium oxalate at higher digestion temperatures to find the maximum allowable temperature. Tables 4.1

Table 4.1: Temperatures During Kjeldahl Digestion Necessary for Determination of Nitrogen in Tar Bases (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society).

Digestion temperature after 1 hour (°C)	Nitrogen (%)
358	8.28
368	8.90
381	8.90
405	8.90
424	8.62

Table 4.2: Retention of Ammonium Ions of Ammonium Oxalate at High Kjeldahl Digestion Temperatures (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society).

Digestion temperature (°C)		Apparent nitrogen (%)
After preboil	After 60-minute digestion	
322	322	19.61
353	351	19.63
399	401	19.62
445	515	8.05
515	[a]	13.11

[a] Digest solidified after 32 minutes so digestion was stopped.

and 4.2 indicate that the maximum is slightly above 400°C.

Lake and co-workers also identified the amount of sulfuric acid consumed by various materials (Table 4.3) and the effect of barometric pressure on digestion temperature (Figure 4.2). Their results indicate the need to fine-tune the analysis for each application and within

Table 4.3: Consumption of Sulfuric Acid during Kjeldahl Digestion by Different Type Samples[a] (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society).

Sample description	Net loss of H_2SO_4 due to sample[b,c] (g)	Final digestion temperature (°C)
Dodecane	0.5	367
Methylcyclohexane	0.6	368
Sucrose	6.7	377
Shale oil naphtha	10.0	381
Petroleum (paraffinic)	13.4	389
Shale oil light gas oil	15.7	385
Shale oil naphtha tar base	15.7	399
o-Xylene	16.6	388
Crude shale oil	18.4	394
Dodecene	19.9	398

[a] 1 ± 0.05-gram samples, 30 mL of sulfuric acid, 1.3 grams of mercury, and 25 grams of potassium sulfate.

[b] Observed weight loss during digestion minus sample weight minus no-sample digestion weight loss.

[c] Average of two or more determinations.

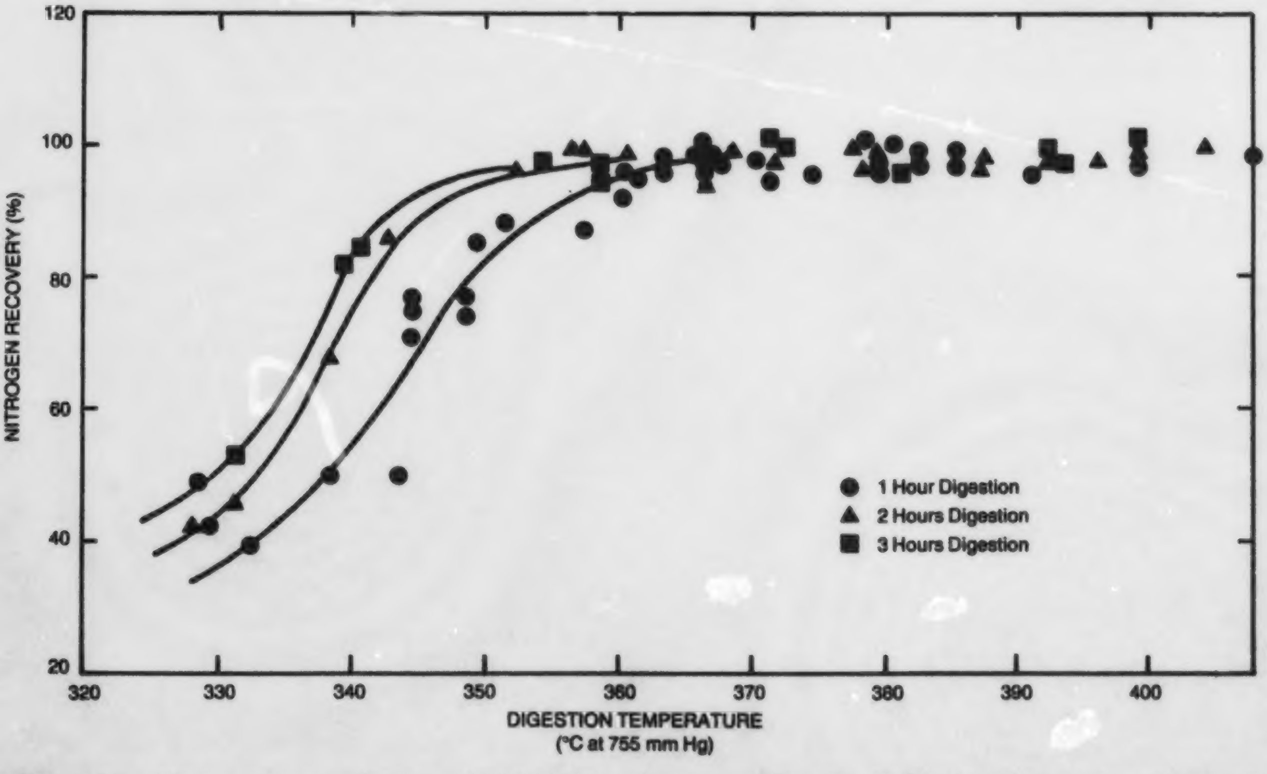

Figure 4.1: Nitrogen Recovery During a Kjeldahl Determination as a Function of Digestion Temperature (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society.)

Table 4.4: Kjeldahl Method Accuracy (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society).

Sample	Nitrogen (%)		% of theoretical actually found
	Calculated	Found	
Pyridine (99.91 mole %)	17.696	17.55	99.2
Pyridine (99.91 mole %) + toluene	4.244	4.192	98.8
Pyridine (99.91 mole %) + toluene	0.817	0.815	99.8
Petroleum naphtha with added nitrogen[a]	1.09	1.11	101.8
Petroleum naphtha with added nitrogen[b]	0.99	1.02	103.0
Petroleum naphtha with added nitrogen[c]	0.93	0.94	101.0

[a] From pyrrole and 2,4,6-trimethylpyridine.

[b] From 1-methylpyrrole and 2,4,6-trimethylpyridine.

[c] From 2,5-dimethylpyrrole and 2,4,6-trimethylpyridine.

each laboratory to maintain the required digestion conditions. They also verified the accuracy of the Kjeldahl-Wilfarth-Gunning method by analyzing mixtures of toluene or naphtha and nitrogen compounds (Table 4.4).

Most nitrogen in petroleum samples is in a form which can be measured by the Kjeldahl-Wilfarth-Gunning method. Nitro compounds, which can only be measured after pretreatment with a reducing agent such as o-mercaptobenzoic acid or a mixture of sodium thiosulfate and salicylic acid,[17] are not usually present. Azo, hydrazine and pyrazole compounds which convert to nitrogen during digestion cannot be recovered. The ACOSA cooperative study (Table 4.5) showed no significant difference between the Kjeldahl and other methods for determining nitrogen in Athabasca bitumens and Lloydminster heavy oils. The Phillips study did yield lower results when the Kjeldahl method was used for analysis of California and Maya crudes.[15] The lack of conclusive evidence from the two studies could be a reflection of either the small number of data points from which the means were calculated or differences in the types of nitrogen compounds in the two sets of samples.

The Dumas Method and Elemental Analyzers

The previous section has shown that the Kjeldahl analysis may give low nitrogen values due to the refractory nature of some nitrogen compounds, or it may cause loss of nitrogen as elemental nitrogen or nitrogen oxides from others. The classical Dumas method, with a volumetric measurement of nitrogen gas, tends to yield high results if gases other than elemental nitrogen enter the nitrometer. These include neutral gases such as methane and acetylene which are sometimes produced during combustion and are not removed by alkali scrubbers. Carbon dioxide, a major product of combustion, will also enter the nitrometer if it is not completely removed by the alkali scrubber. The carbon dioxide required to sweep the nitrogen oxides which adsorb on the copper oxide in the combustion tube must be of the highest purity to prevent contamination. Incomplete reduction of

Figure 4.2: Control of Digestion Temperature by Varying the Amount of Potassium Sulfate (Reprinted with permission from Anal. Chem. 1951, 23, 1634-1638. Copyright 1951, American Chemical Society).

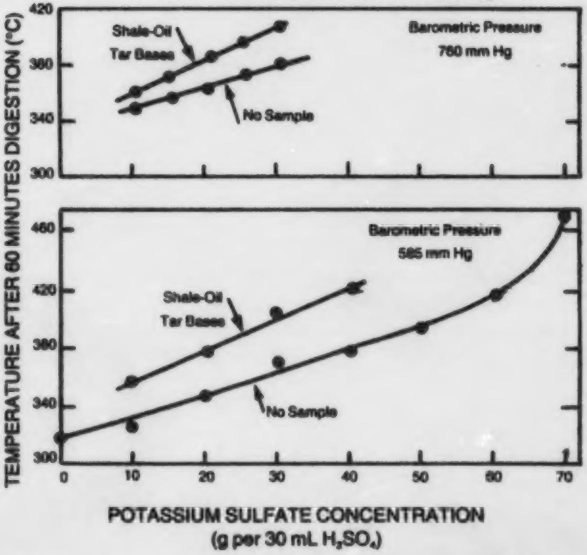

Table 4.5: Comparison of Kjeldahl with Chemiluminescence and Dumas Results from Two Cooperative Studies

	Nitrogen		
	Kjeldahl	Dumas	Chemiluminescence
ACOSA			
Athabasca bitumen	0.432	0.443	0.453
Lloydminster heavy oil	0.315	0.320	0.345
Phillips			
California heavy oil	0.517	0.592	0.580
Maya crude	0.324	0.359	0.353

nitrogen oxides to nitrogen also results in an error as NO has only half as much nitrogen as a similar volume of N_2. Van Meter and co-workers analyzed combustion gases from the Dumas method by mass spectrometry and determined their effect on nitrogen values for shale oil products and synthetic mixtures.[20] Their data are reproduced in Tables 4.6 and 4.7. Their study arose from an interlaboratory exchange of samples for nitrogen determinations reported in 1951. The results of this exchange, summarized in Table 4.8, led the organizers to conclude that the high values from the Kjeldahl analyses and low values from the Dumas analyses were probably the closest to the true nitrogen contents of the samples.[1]

These sources of error were not always recognized and some analysts assumed that, in the case of discrepancies between the Kjeldahl and Dumas methods, the former was in error because of its known potential for

Table 4.6: Dumas Microanalyses of Shale Oil and Fractions (Reprinted with permission from Anal. Chem. 1951, 23, 1638-1639. Copyright 1951, American Chemical Society).

	Nitrogen (%)			
	Uncorrected	Corrected[a]	Nitric oxide (%)	Hydrocarbons (%)
Crude shale oil	2.00	1.86	0.8	6.7
	1.95	1.93	0.9	0.8
	2.27	2.03	0.7	10.3
		$\bar{x}$ = 1.94		
Diesel fraction from shale oil	1.89	1.64	1.1	12.9
	1.79	1.64	1.2	7.8
	1.92	1.64	1.1	14.3
		$\bar{x}$ = 1.64		
Shale oil naphtha	1.67	1.14	0.3	29.4
	2.25	1.04	0.6	53.6
	1.74	0.89	1.2	48.3
		$\bar{x}$ = 1.02		

[a] Corrected for hydrocarbon gases and NO which was produced during combustion but not converted to N_2.

Table 4.7: Dumas Microanalyses of Synthetic Oils (Reprinted with permission from Anal. Chem. 1951, 23, 1638-1639. Copyright 1951, American Chemical Society).

	Nitrogen (%)				
		Found			
	Calculated	Uncorrected	Corrected[a]	Nitric oxide (%)	Hydrocarbons (%)
2,6-Dimethylquinoline-n-hexadecane	1.74	1.98	1.69	0.1	15.3
		2.32	1.65	0.0	28.9
		3.42	1.77	0.2	47.9
		1.85	1.85	0.0	0.0
		1.75	1.75	0.1	0.0
4-(5-Nonyl)pyridine-n-hexadecane	0.74	0.69	0.69	0.3	0.2
		0.80	0.80	0.7	0.2
		0.73	0.72	0.9	1.6
Pyrrole-iso-octane-toluene	1.97	2.30	2.01	0.0	12.5
		2.35	2.00	0.2	15.0
Quinoline-n-hexadecane-toluene	0.38	0.44	0.44	1.9	0.1
		0.43	0.41	1.0	3.8
Quinoline-toluene	3.70	3.87	3.87	0.0	0.0
		3.88	3.87	0.1	0.1

[a] Corrected for hydrocarbon gases and NO which was produced during combustion but not converted to N_2.

Table 4.8: Nitrogen Values Reported from an Exchange of Shale Oil Samples (Reprinted with permission from Anal. Chem. 1951, 23, 1632-1634. Copyright 1951, American Chemical Society).

	Nitrogen (%)								
	Crude shale oil			Shale oil naphtha			Shale oil diesel fuel		
	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
Kjeldahl									
Macro	1.15	2.10	1.82	0.64	1.02	0.89	1.31	1.67	1.54
Micro to Semi-micro	1.43	2.18	1.84	0.55	1.41	0.96	1.00	1.79	1.48
Dumas									
Macro	1.80	1.82	1.81	0.85	0.92	0.89	1.59	1.79	1.69
Micro to Semi-micro	1.74	2.41	2.06	0.94	2.17	1.34	1.45	2.04	1.77

nitrogen loss. Mabery, for example, assumed the Dumas nitrogen values for several oils from California given in Table 4.9 were correct.[12] Subsequent work showed that the Kjeldahl values were more accurate but that the Dumas method, if carried out correctly, could also yield reliable data.

Table 4.9: Mabery's Analyses by Kjeldahl and Regular Dumas Methods[12]

	Nitrogen (%)	
	Kjeldahl	Dumas
Los Angeles County		
(a)	0.47	1.42
(b)	0.69	1.52
Ventura County		
(a)	0.64	1.91
(b)	0.71	2.39
Summerland	0.88	2.10

Elemental analyzers which rely on thermal conductivity detection of nitrogen avoid the potential for error which accompanies volumetric measurement of nitrogen. With these analyzers, the keys to a good analysis lie in complete combustion of the sample, sweeping of the nitrogen oxides from the catalyst and reduction of the oxides to elemental nitrogen.

Comparisons have been reported for data from an elemental analyzer (the Perkin-Elmer 240) using a thermal conductivity detector and the Kjeldahl method[18] (Tables 4.10 and 4.11). The large relative errors between the two methods reported in Table 4.11 can be explained by the repeatability of the Kjeldahl method which is $0.066(\%N)^{1/2}$ over the range of 0.015 to 2% nitrogen. The LECO CHN-600 elemental analyzer uses a much larger test sample (~ 150 mg) than either the Carlo Erba or Perkin-Elmer analyzers which use about 1.5 mg of material. Any improvement in precision in the LECO instrument compared to the Perkin-Elmer analyzer would have to be attributed to design rather than due to reduction in sampling uncertainty.

Table 4.10: Analysis of Baja Crude (Reprinted with permission from Mikrochim. Acta [Wien] 1972, 217-222).

Nitrogen (%)	
Kjeldahl	PE-240
0.40	0.34
0.37	0.33
0.38	0.35
0.37	0.31
0.36	0.31
$\bar{x}$ = 0.38	$\bar{x}$ = 0.33
s = 0.02	s = 0.02

Table 4.11: Analysis of Nitrogen in Petroleum Products (Reprinted with permission from Mikrochim. Acta [Wien] 1972, 217-222).

	Nitrogen (%)		Deviation from Kjeldahl
	Kjeldahl	PE-240	(% Relative)
Dewaxed oil	0.040	0.057	42.5
charge	0.046	0.064	39.1
Hydrotreated	0.073	0.075	2.7
resid	0.084	0.075	10.7
450 Bottoms	0.070	0.050	28.5
	-	0.045	-
Hydrogenated	0.055	0.059	7.3
gas oil	0.071	0.055	22.5
Hydrogenated	0.070	0.066	5.7
gas oil	0.064	0.060	6.3

The data from the chapter describing determination of ash suggests that for 1.5-mg increment sizes, the variability in ash level is approximately 0.25% for a material with 0.5% ash. The following analysis of propogation of errors indicates that use of the larger increments for the purpose of decreasing sample variability does not improve precision.

$$\%N_{\text{pure bitumen}}\,(x) \times (1\text{-wt. fraction ash }(y)) = \%N_{\text{bitumen plus solids}}\,(z)$$

$$\text{or} \quad z = x(1-y) \qquad (1)$$

For a bitumen sample containing 0.4% nitrogen and approximately 0.5% solids, Δz, the standard deviation of an analysis is approximately 0.03%. The uncertainty of $\Delta(1\text{-}y)$ equals 0.0025 for a 1.5-mg test sample. Therefore the uncertainty in the analysis of a 1.5-mg test sample of a pure bitumen containing no solids (Δx) is 0.03 because

$$\Delta z = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{1-y}\right)^2}\ |z| \qquad (2)$$

$$0.03 = \sqrt{\left(\frac{\Delta x}{0.4}\right)^2 + \left(\frac{.0025}{.995}\right)^2} \times 0.4$$

$$\Delta x = 0.03$$

This is the same as the uncertainty in the analysis of a bitumen containing 0.5% solids. Given Δx equals 0.03, Δz would increase to 0.04 only if Δy equalled 0.09. For Δy to equal 0.09, the standard deviation in the solids determination for a sample containing 0.5% solids need to be 9%. On a molecular level, increasing the test sample size from 1.8×10^{18} molecules (1.5 mg) to 1.8×10^{20} molecules (150 mg) is also unlikely to reduce sampling error.

Optimization of Operating Conditions for Chemiluminescence Analyzers.

The chemiluminescent nitrogen detector originally patented by Parks in 1977,[14] was evaluated by Drushel[6] specifically for determination of nitrogen in petroleum fractions. He documented the effect of gas flow rates, sample introduction rates and combustion temperatures on response for samples which could be injected by syringe and residual fuels introduced to the pyrolysis chamber in a sample boat.

Varying the oxygen, helium and gas flow rates from less than 50 to 325 mL/min. had little effect on response. However, the shape of the calibration curve for 9-methylcarbazole in toluene varied considerably with sample boat introduction rate. By adopting a introduction rate of 0.25 in./min., the linear range could be extended up to 500 µg N/mL (Figure 4.3). Drushel provided a plot relating response to nitrogen concentration for a sample of shale oil bottoms dissolved in toluene, but a direct comparison with the curves for 9-methylcarbazole could not be made because of differences in operating conditions.

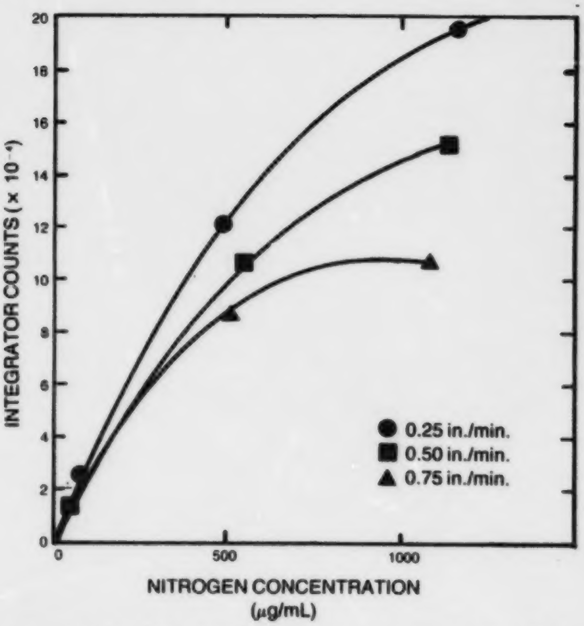

Figure 4.3: Effect of Sample Boat Introduction Rate on Detector Response for a Chemiluminescence Analyzer

Gas flow rates: He, 80 mL/min.; O_2, 240 mL/min.; O_3, 240 mL/min.

Sample size: 4 mL of 9-methylcarbazole in toluene (Reprinted with permission from Anal. Chem. 1977, 49, 932-939. Copyright 1977, American Chemical Society).

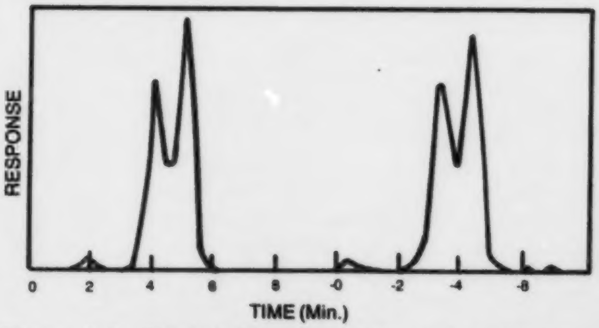

Figure 4.4: Typical Response Curve for a Quartz Boat Inlet System in a Chemiluminescence Analyzer Sample: Atmospheric Residum (dissolved in toluene) (Reprinted with permission from Anal. Chem. 1977, 49, 932-939. Copyright 1977, American Chemical Society).

Drushel also reported increased detector response up to 850°C; above this temperature increases in response were marginal. The necessity of keeping the temperature at 850°C was demonstrated by a typical response curve for an atmospheric residum given in Figure 4.4. He attributed the two peaks to differences in volatility of the nitrogen compounds.

Table 4.12: Effect of Compound Type on Response from Chemiluminescence and Coulometric Analyses

	Nitrogen recovery (%)		
	From reference 6[a] (chemiluminescence)	From reference 10[b] (chemiluminescence)	From reference 13[c] (microcoulometry)
Pyridine	106	105	100.9
Quinoline	99	-	-
3.4-Benzoquinoline	103	-	-
8-Hydroquinoline	-	97	-
Indole	104	-	102
Azobenzene	11	45	97
Nitrobenzene	73	98	103
N-Nitrosodiphenylamine	72	101	-

[a] 9-methylcarbazole was used as a standard. (Reprinted with permission from Anal. Chem. 1977, 49, 932-939. Copyright 1977, American Chemical Society.

[b] Benzoquinoline was used as a standard. Each result is an average of eight determinations. (Reprinted with permission from Mikrochim. Acta. [Wien] 1980 II, 455-463.

[c] Reprinted with permission from Anal. Chem. 1966, 38, 1209-1213. Copyright 1966, American Chemical Society.

Drushel's work on chemiluminescence included an evaluation of the effect of compound type on response, (Table 4.12), and comparisons of chemiluminescence with coulometric and Kjeldahl determinations for nitrogen in residua and gas oils (Table 4.13). Table 4.12 shows that Drushel's chemiluminescent method is unsuitable for nitro and azo compounds. Chemiluminescence does, however, provide data equivalent to the Kjeldahl method for most petroleum samples. Low nitrogen values may be obtained if coke is produced during pyrolysis as indicated by coke buildup in the exit tube outside the pyrolysis chamber.

In Drushel's evaluation, pyrolysis took place in a quartz combustion tube at ~ 850°C. Kunkel and Geldermann found that the use of a cobalt oxide-tungsten oxide oxidation catalyst in the pyrolysis tube at 1000°C followed by a graphite tube to reduce NO_2 to NO:

$$NO_2 + C \rightarrow NO + CO$$

resulted in improved, but not necessarily complete, detection of nitrogen in nitro and azo compounds[10] (Table 4.12). These changes also caused expansion of the linear range to 1 to 30,000 mg/kg of nitrogen and a four-fold increase in sensitivity. Kunkel and Gelderman verified the accuracy of their method by analyzing standard compounds and petroleum products using the chemiluminescence and Kjehdahl methods (Tables 4.14 and 4.15).

Determination of Nitrogen by Microcoulometry

Before the advent of chemiluminescence, Martin had described the coulometric method for measuring nitrogen.[13] Like Drushel and Kunkel, he verified the accuracy of the method by analysis of standard compounds (Table 4.12) and compared his method to the Kjeldahl method for petroleum fractions (Table 4.16). He acknowledged that compounds boiling above the kerosene range failed

Table 4.13: Comparison of Chemiluminescence with Kjeldahl Results Unless otherwise stated, each result is the mean of four determinations. (Reprinted with permission from Anal. Chem. 1977, 49, 932-939. Copyright 1977, American Chemical Society).

Residuum or gas oil sample no.	Nitrogen (%)		Deviation from Kjeldahl (% relative)
	Chemiluminescence[a]	Kjeldahl	
593622	0.2794	0.2619	+ 6.68
593643	0.3502	0.3766	− 7.01
593652	0.4012	0.4004	+ 0.20
593686	0.3385	0.3487	− 2.93
593688	0.2789	0.2955	− 5.62
608001	0.2354	0.2314	+ 1.73
608034 (502)	0.7934	0.8362	− 5.12
414338	0.0995	0.0914	+ 8.86
414174	0.1069	0.0847	+26.21
583790 (502)	0.3562	0.3544	+ 0.51
608037 (502)	0.5372	0.5514	− 2.58
583780 (502)	0.4233	0.4372	− 3.18
583758 (502)	0.4070	0.4290	− 5.13
609029	0.3990	0.3989	+ 0.03
607999	0.3939	0.4281	− 7.99
Qual. control atm. resid.	0.2759[c]	0.2680	+ 2.95
Atm. resid. 1	0.4495[d]	0.469[b]	− 4.16
Atm. resid. 2	0.9208[d]	0.944[b]	− 2.46
Distillate gas oil	0.1878[d]	0.183[b]	+ 2.62

[a] Oven temperatures: Inlet, 950°C; center, 880°C. Gas flow rates: O_2, 120 mL/min; He, 70 mL/min. Boat introduction rate: 0.25 in./min.

[b] Average of values from four different laboratories.

[c] Mean of three determinations.

[d] Mean of two determinations.

Table 4.14: Comparison of Chemiluminescence and Kjeldahl Method for Standard Compounds (Reprinted with premission from Mikrochim. Acta [Wien] 1980 II, 455-463.)

	Nitrogen recovery (%)	
	Chemiluminescence	Kjeldahl
Atropine	101	60
2-Aminoanthracene	96	74
4-Azafluorene	100	27
Phenylbenzimidazole	92	90
2,1-Dinitrophenyl-hydrazone	68	58
m-Nitroaniline	99	67
Indazole	102	39

Table 4.15: Comparison of Methods Used for the Analysis of Petroleum Products (Reprinted with premission from Mikrochim. Acta [Wien] 1980 II, 455-463.)

	Nitrogen content		
	Chemiluminescence	Kjeldahl	Carlo Erba Elemental Analyzer
Kerosene	39 mg/kg	45 mg/kg	
Petroleum fraction	105	81	
Fuel oils	97	95	
	83	95	
Gasolines	320	332	
	20	20	
Crude benzene	0.35%	0.33%	0.1 %
Distillation residue	0.52	0.33	0.65
Oil shale	0.19	0.15	0.55
Fuel oil	0.36	0.33	
	0.52	0.47	
Coal oil-fractions	0.29	0.30	0.2
	0.53	0.56	0.5
	1.33	1.28	1.0

to yield ammonia quantitatively due to coke formation on the hydrogenation catalyst (nickel on magnesia) even at the relatively high temperature of 440°C. At a critical level of catalyst deactivation, ammonia production drops rapidly.

Rhodes, Hopkins and Guffy extended the range of materials which could be analyzed to 800°C by modifying the electrode system as well as using a nickel catalyst instead of a nickel on magnesia catalyst to produce ammonia.[16] Their comparison of the improved coulometric method with the Kjeldahl method for a variety of petroleum products is given in Table 4.17.

Zeen and Van Grondelle found that mixing test samples of coals, residua and heavy oils with lithium hydroxide resulted in complete liberation of the nitrogen which would have been trapped in the char under normal operating conditions.[23] The lithium hydroxide probably acts by forming carbon monoxide and lithium carbide from the char:

$$2\ \mathrm{LiOH} + 3\mathrm{C} \rightarrow \mathrm{CO} + \mathrm{Li_2C_2} + \mathrm{H_2O}.$$

The carbide reacts with water:

$$\mathrm{Li_2C_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{LiOH} + \mathrm{C_2H_2}$$

so the char is completely converted to gases and the occluded nitrogen is released. They proved the value of this modification by comparing Kjeldahl and microcoulometric analyses of coals, residua and heavy oils. These comparisons appear in Table 4.18.

SUMMARY

When new methods for determining nitrogen are being developed, researchers generally use the Kjeldahl method as a referee. The types of nitrogen compounds which cannot be measured in the Kjehdahl test, are usually found at low levels, if at all, in petroleum products. As extensive descriptions of the method are available, a laboratory should, after practice, be able to produce accurate data.

The Kjeldahl test is not always the method of choice due to the long time required for an analysis. Although

Table 4.16: Comparison of Kjeldahl and Microcoulometric Methods for Analysis of Petroleum Fractions (Reprinted with permission from Anal. Chem. 1966, 38, 1209-1213. Copyright 1966, American Chemical Society).

	Nitrogen (mg/kg)		Deviation from Kjeldahl
	Kjeldahl	Microcoulometry	(% relative)
Shale naphtha	1900	1920	+ 1.1
Light catalytic cycle oil	241	233	− 3.3
Heavy virgin gas oil	605	600	− 0.8
Catalytic naphtha	0.5[a]	0.8	+60
Percolated heavy cycle oil	2[a]	1.7	−15

[a] Analysis made after prior concentration; estimated uncertainty about ± 50% relative.

Table 4.17: Comparison of Kjeldahl and Modified Microcoulometric Methods for Analysis of Petroleum Fractions (Reprinted with permission from Anal. Chem. 1971, 43, 556-561. Copyright 1971, American Chemical Society).

	Final boiling point (°C)	No. of microcoulometric analyses	Nitrogen (mg/kg)		Deviation from Kjeldahl (% Relative)
			Microcoulometric	Kjeldahl	
Processing product	445	4	0.28 ± 0.02	0.25	+12.0
Processing product	520	15	11.5 ± 0.4	12	− 4.2
Processing product	545	3	0.19 ± 0.0	0.21	− 9.5
Processing product	545	4	0.08 ± 0.02	<0.1	—
Furnace oil	~340	2	99.3 ± 0.5	100	− 0.7
Processing stock	550	4	1015 ± 42	991	+ 2.4
Atmospheric residuum (1 wt % S)	>540	1	1715	1740	− 1.4
Vacuum bottom	>540	1	1730	1740	− 0.6
Lubricating oil blend	—	1	352	340	+ 3.5
Butene gas	-	1	19	16	+18.8
Olefin-amine copolymer	MW > 10,000	4	1160 ± 18	1080	+ 7.4

Table 4.18: Comparison of Results Obtained by the Microcoulometric - Flux Method and the Kjeldahl Method (Reprinted with permission from Mikrochim. Acta 1980, 118, 227-283.)

	Nitrogen (%)		
	Kjeldahl	Microcoulometer	
		With flux	Without flux
Coal A	1.72	1.78	1.20
Coal B	1.69	1.75	-
Coal C	1.58	1.64	-
Coal D	0.36	0.34	-
Coal E	0.43	-	
0.41			
Coal F	1.05	1.06	0.80
Coal G	1.70	1.69	1.04
Heavy crude oil A	0.57	0.59	0.52
Heavy crude oil B	0.59	0.58	0.55
Vacuum dist. residue A	0.44	0.45	0.40
Vacuum dist. residue B	0.82	0.83	0.50
Vacuum dist. residue C	0.35	0.40	0.35
Asphaltenes from a long residue	0.66	0.70	0.46

there is considerable concern in the industry about using chemiluminescence for high-boiling-point materials, the ACOSA and Phillips studies, as well as individual researchers indicated that chemiluminescence and the Kjeldahl test produce equivalent results for heavy crudes.

The Dumas method is also used successfully for samples with high nitrogen levels (>0.3%).

The combustion stage in the microcoulometric test has been modified recently for heavy materials but high maintenance requirements of the titration cell are still a serious concern.

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Chapter 5: OXYGEN

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OXYGEN

DEFINITION

Oxygen is one of the five major elements in heavy oil.

SIGNIFICANCE

The oxygen content of well-preserved bitumens and heavy oils rarely exceeds 1.5%. Even this level is critical because upgraders and refiners have little experience with crudes containing oxygen above trace levels.

The effect of oxygen on a recovery or upgrading process depends on the type of oxygen compound rather than the absolute amount in a crude. If present as a carboxylic acid, oxygen may be beneficial to in-situ oil recovery due to lowering of the interfacial tension between oil and water.[10] In the hot water process, a maximum recovery of bitumen has been related to critical levels of surfactants which are derived from carboxylic and sulfonic acids in the bitumen.[14] The presence of high levels of carboxylic acids can lead to formation of hard-to-break emulsions in both in-situ recovery and hot water extraction.

Phenolic compounds can undergo condensation reactions during upgrading to form polymers and stable ethers that survive coking and accumulate on hydrotreating catalysts.[10] Guard reactors are sometimes required to protect these catalysts. Phenolic compounds also cause difficulties in the treatment of produced waters.

METHODS

1. Automated Elemental Analysis by Pyrolysis

1.1 Application

Elemental analyzers used to measure carbon, hydrogen and nitrogen can be converted to perform analyses for oxygen in heavy crudes. Estimates of the limits of detection by this method vary widely but some are as low as 0.01%.

1.2 Summary of the Method

A test sample weighing several milligrams is pyrolyzed in a quartz tube containing platinized carbon to convert the oxygen to carbon monoxide. In the Carlo Erba elemental analyzer, the carbon monoxide is separated from the other pyrolysis gases on a 5Å molecular sieve and measured by a thermal conductivity detector (TCD). In the Perkin-Elmer analyzer, the carbon monoxide is converted to carbon dioxide over copper oxide before being measured by a TCD. The detector responses for test samples are compared to a standard calibration curve.

1.3 Precision

	Repeatability (%)	Reproducibility (%)
ACOSA[a]	0.3	> mean oxygen content
Smith[b]	0.13 (classical) 0.21 (automated)	

[a] From triplicate analyses by four laboratories of an Athabasca bitumen and a Lloydminster heavy oil. Repeatability was similar to the manufacturer's specifications for the equipment, yet the reproducibility was greater than the mean oxygen content (~1.2%) determined by difference by thirteen laboratories.

[b] Calculated from 2.83 times the pooled standard deviation from pairs of data in Table 5.2.

2. Neutron Activation Analysis (NAA)[4,7]

2.1 Application

Fast neutron activation analysis can be used to measure the level of oxygen in fossil fuels.

2.2 Summary of the Method

A test sample is exposed to 14-MeV neutrons produced by the $^{3}H(d,n)^{4}He$ reaction in a neutron generator. These neutrons cause the $^{16}O(n,p)^{16}N$ nuclear reaction via the metastable ^{17}O intermediate. ^{16}N has a half-life of 7.1 seconds and emits 6.13- and 7.1-Mev gamma rays which are detected by NaI(Tl) scintillation detectors. Responses are compared to those for standard samples.

2.3 Precision

Data from the analysis by Khalil and co-workers of various coal liquid products were used to estimate repeatability.[7]

Coal Liquid	Oxygen (%)	Repeatability (%)
Atmospheric still overhead	1.42	0.25
Atmospheric still bottom	1.70	0.25
Vacuum still overhead	1.50	0.25
Vacuum still bottom	9.48	0.82
Shale oil retort liquid sample	1.46	0.13
Coal liquid product	5.16	0.19
Filtered liquid product	3.88	0.19
Liquid filtrate	28.89	2.47

Atomic Energy of Canada Ltd. in Pinawa, Manitoba reports a precision of 5% relative at the 95% level of confidence with a detection limit of 1 mg in samples up to 27 mL, or approximately 40 mg/kg.[6]

DISCUSSION

Review of Oxygen Analysis by Pyrolysis

Accurate estimates for oxygen are more difficult to obtain than for the other major elements in heavy crudes. Direct measurements at low levels are prone to such large errors that few laboratories measure oxygen directly, and those that do cannot provide comparable results. In the ACOSA cooperative study, estimates of oxygen content by difference were more reproducible, although not necessarily more accurate, than those obtained by direct measurement.

Analysts have recognized that the uncertainty in a measurement by difference includes the uncertainties in the measurements of other components in the sample and have attempted to develop a direct method suitable for a variety of materials. The following review of the work leading to modern elemental analyzers should provide an appreciation of possible sources of error in an oxygen determination, with emphasis on the stability of catalysts and adsorbers and interferences caused by hydrogen, nitrogen and sulfur.

The direct measurement of oxygen was developed by Schutze (1939) who pyrolyzed the test sample in a stream of nitrogen, and passed it over carbon at 1000°C to convert the oxygen to carbon monoxide.[16] The carbon monoxide was then converted to carbon dioxide, adsorbed in a trap and weighed.

Unterzaucher (1940) modified the Schutze method by raising the pyrolysis temperature to 1120°C.[18] The carbon monoxide was reacted with iodine pentoxide at 125°C to produce elemental iodine and carbon dioxide. The iodine was oxidized to iodate, reduced to free iodine and determined by titration with a standard solution of 0.2N sodium thiosulfate. Samples containing sulfur produced acidic gases such as H_2S which were removed by adsorption on Ascarite before they could pass over the iodine pentoxide and liberate iodine.

Maylott and Lewis (1950) found that during pyrolysis of samples containing sulfur, some non-acidic gases such as carbon disulfide (CS_2) and carbonyl sulfide (COS) were produced.[9] These gases were not adsorbed by Ascarite. They were produced with H_2S in various proportions depending on the nature of the test sample, thereby precluding the use of a correction factor. Maylott and Lewis used a liquid nitrogen trap to remove the neutral gases. This strategy posed a problem because the carbonyl sulfide would liberate iodine if not removed but at the same time, it contained oxygen from the sample which would not be measured when a nitrogen trap was employed. They recommended that the amount of COS in the trap should be determined but an appropriate analytical method was not identified.

Dundy and Stehr (1951) showed that hydrogen gas was a major product of pyrolysis and that iodine was liberated from iodine pentoxide in the presence of hydrogen and carbon monoxide at temperatures as low as 100°C.[3] They concluded that in a titrimetric determination, high oxygen values would be obtained due to the effect of hydrogen, and a gravimetric determination of CO_2 as originally proposed by Schutze was more appropriate. Dundy and Stehr also considered the problems of sulfur-bearing samples. Carbon disulfide and carbonyl sulfide produced SO_3 and CO_2 in the oxidation and iodine absorption tubes; this CO_2 would contribute to high oxygen values. Therefore, like Maylott and Lewis, they used liquid nitrogen traps to remove these interferences.

Table 5.1: Comparison of Methods for Removing Sulfur Interference in Oxygen Analysis Using 50% Platinized Carbon at 900°C (Reprinted with permission from Anal. Chem. 1954, 26, 600- 602. Copyright 1954, American Chemical Society.)

	Oxygen (%)			
	Actual	Found		Sulfur (%)
		Decomposition of CS_2 and COS over Cu	Liquid Nitrogen trap	
Thiourea	0.00	0.16, 0.06	0.06	42.0
Mixtures of mesitylene, benzyl disulfide and benzoic acid	0.53	0.42, 0.51	0.26, 0.25	1.6
	0.99	1.10, 0.91	0.45, 0.66	1.0
	2.34	2.26, 2.30	0.53, 0.77	2.2
Mixture of mesitylene, $C_{11}H_{12}N_2S_3$[a] and benzoic acid	1.60	1.67, 1.65	0.53, 0.73	1.3
Mixture of mesitylene, $C_{11}H_{12}$-N_2S_3[a] and maleic anhydride	5.04	4.96, 5.00	4.27, 4.03	1.3
Cystine	26.65	26.66 ± 0.06[b]	25.4	26.7
Sulfanilic acid	27.72	27.69 ± 0.07[c]	25.6, 24.3	28.5

[a] Contains thiol and thioether groups.

[b] Average of four analyses.

[c] Average of seven analyses.

Even with trapping of the sulfur gases, unexplained systematic errors in the analysis of oxygen remained. Oita and Conway[12] pointed out that Maylott and Lewis trapped enough COS during the analysis of 2-thiobarbituric acid to account for 0.48% of the oxygen, yet their experimental value without correction was only low by 0.14%. Dundy and Stehr trapped the equivalent of 0.1% oxygen in cystine but their analytical data was 0.1% high. Henkel and Raymond also found high results for cystine.[5] They attributed the error to release of oxygen from the silica tube wall by sulfur in the pyrolysis gases.

Oita and Conway (1954) attempted to eliminate this complication by operating the pyrolysis tube at a lower temperature.[12] They substituted a platinum-carbon mixture for the pure carbon catalyst and were able to lower the pyrolysis temperature to the range of 700 to 900°C. By doing so, they practically eliminated the formation of oxygen compounds from the reaction of carbon with the quartz tube. The CS_2 and COS produced during pyrolysis were decomposed by passing the pyrolysis gases over copper at 900°C where the following reactions probably occurred:

$$4\ Cu + CS_2 \rightarrow 2Cu_2S + C \text{ and}$$

$$2\ Cu + COS \rightarrow Cu_2S + CO$$

The nitrogen carrier gas in the system contained sufficient hydrogen to react with Cu_2S to produce H_2S which was trapped on the Ascarite tube before it could react with the I_2O_5 to produce elemental iodine. Carbon monoxide was converted to CO_2 which reacted with I_2O_5 as described previously. By avoiding the use of a liquid nitrogen trap, Oita and Conway obtained accurate oxygen values for mixtures of known compounds (Table 5.1).

With the manual method apparently thoroughly understood, little work took place in development of methods for oxygen until the 1960s when automation became the trend. Boos (1964) reverted to combustion at 1120°C over pelletized carbon and measured the produced carbon monoxide by a thermal conductivity detector (TCD).[1] He analyzed samples that contained sulfur and trapped the

Table 5.2: Analysis for Oxygen in Various Petroleum Products (Reprinted with permission from Mikrochim Acta [Wien] 1972, 217-222.)

	Oxygen (%)		
	Unterzaucher	PE 240	Deviation from Unterzaucher (% Relative)
Sludge	5.69	5.82	0.0
	5.76	5.64	
Bitumen	1.05	1.05	+ 3.8
	1.03	1.11	
Texas beach residue	1.03	1.10	+ 7.4
	1.14	1.22	
Heavy gas oil	0.43	0.42	0.0
	0.45	0.45	
Heavy gas oil	0.87	0.94	+ 14.3
	0.81	0.98	
Phenol in transformer oil	1.04[a]	1.08	+ 2.9
		1.05	
Phenol in transformer oil	0.58[a]	0.56	0.0
		0.60	
Phenol in transformer oil	0.20[a]	0.21	0.0
		0.19	

[a] Calculated from the known addition of phenol.

H_2S produced during pyrolysis on Ascarite. Culmo (1968) automated the approach of Oita and Conway by pyrolyzing the sample in helium over platinized carbon at 950°C.[2] He then passed the carbon monoxide over CuO at 610°C and measured the produced CO_2 by TCD.

Smith and co-workers (1972) compared analytical data obtained from the Perkin-Elmer elemental analyzer with the classical Unterzaucher method for determining oxygen. They found good agreement for a variety of samples[17] (Table 5.2).

When nitrogenous gases produced during pyrolysis adsorb on the carbon catalyst the nitrogen peak tails onto the CO peak, leading to erroneously high oxygen results. Pella and Andreoni (1976) described the use of a 40% nickelized carbon that reduced the adsorption of nitrogen during pyrolysis.[13] Kirsten (1978) doped his carrier gas, helium, with chloropentane to enhance the liberation of oxygen from the carbon residue of the sample as well as the carbon catalyst.[8] By doing so, he was able to lower the pyrolysis temperature from 1120°C to 1020°C.

Oita (1984) further refined the automated analysis to overcome problems caused by samples with high levels of metals.[11] During pyrolysis metals may be deposited on the carbon catalyst and are oxidized by air entering the system as the sample is being inserted. The metal oxides are reduced by hydrogen created during pyrolysis and the water that is formed reacts with the carbon to produce carbon monoxide. This source of CO cannot be distinguished from the CO produced from the oxygen in the sample.

Oita used hydrogen as a carrier gas rather than inert helium or nitrogen to keep any metal deposited on the carbon in a reduced state so it would not contribute to carbon monoxide production. Carbon monoxide from the pyrolysis was measured by a non-dispersive IR detector. His work suggests that the use of nickelized carbon can contribute to positive errors in an oxygen determination.

Activation Analysis

Activation analysis avoids most of the problems of interferences which plague the pyrolysis methods. The major drawback to this method, aside from capital cost, is matrix matching of standards with unknowns. Ehmann stated that for fast neutron activation analysis, samples and standards should be similar with respect to oxygen content, macroscopic density, physical state and mean atomic number to minimize errors due to instrumental dead times and neutron and gamma ray absorption.[4] Ehmann's work suggests that known mixtures of alcohols and ethers in solvents may be suitable as standards for oil analysis. No primary reference standards now exist.

Charged particle activation analysis (CPAA) is similar to NAA except that the bombarding particle is an ion or a proton instead of a neutron.[15] A summary of possible activation reactions for determining oxygen is provided in Table 5.3. CPAA is the only technique available for oxygen measurements at the ultra-trace level; the complexity of the equipment limits CPAA as a routine method even more than NAA.

Table 5.3: Survey of CPAA Procedures for the Determination of Oxygen (Reprinted with permission from Anal. Chem. 1980, 52, 827A-844A. Copyright 1980, American Chemical Society.)

Reaction	Half-life (min.)	Projectile energy (MeV)	Detection limit[a] (ng/g)	Observations
$^{16}O(p,\alpha)^{13}N$	9.96	10	3	b
$^{18}O(p,n)^{18}F$	109.8	10	115	c
$^{16}O(d,n)^{17}F$	1.1	5	40	c
$^{16}O(^3H,n)^{18}F$	109.8	3.5	0.7	c
$^{16}O(^3He,p)^{18}F$ $^{16}O(^3He,n)^{18}Ne \xrightarrow{\beta^+} {}^{18}F$	109.8	15	1.7	d
$^{16}O(^4He,pn)^{18}F$ $^{16}O(^4He,d)^{18}F$ $^{16}O(^4He,2n)^{18}Ne \xrightarrow{\beta^+} {}^{18}F$	109.8	34	2.1	e

[a] For a 10 $\mu A/cm^2$ irradiation at the projectile energy indicated, and a duration equal to one half-life of the radioisotope produced.

[b] Interferences due to C and N cannot be avoided.

[c] Interference-free up to the projectile energy indicated.

[d] Interferences possible from F, Ne, Na, Mg and Al but in practice negligible for E ≤ 15 MeV.

[e] Interferences possible for N, F, Ne, Na, Mg, Al and Si.

Contribution of Contaminants in Test Samples to Systematic Error

Maylott and Lewis reported that in the Unterzaucher method (and therefore presumably in other pyrolysis methods), carbonates are decomposed and metal oxides can be at least partially reduced, leading to high oxygen values.[9] Based upon the findings of Oita, it is probable that water in a test sample forms carbon monoxide and is reported as oxygen. However, there is no evidence available to show if this reaction is quantitative.

Neutron activation analysis will quantitatively measure oxygen in water and inorganic oxides. These contaminants will contribute significantly to the total oxygen content of a bitumen or heavy oil sample if they are not removed prior to analysis.

SUMMARY

The ACOSA cooperative study of 1982 indicated that direct measurements of oxygen were less reproducible than estimates obtained by difference. Sulfur, nitrogen and hydrogen, all of which are present at significant levels in heavy crudes, interfere with oxygen determinations by pyrolysis. Oita's latest work offers some promise in this area.

Neutron activation is unlikely to be used in many laboratories routinely due to the capital expense. When access to a suitable facility exists, NAA may prove to be a practical approach to analysis of batches of samples since it is suited for automated, repetitive analyses. Approximately five replicate measurements are required to reduce the uncertainty in the mean value to an acceptable level. The lack of appropriate standards may also contribute to systematic error.

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Chapter 6: SULFUR

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SULFUR

DEFINITION

Sulfur is one of the five major elements found in bitumen and heavy oil. It is present in the form of compounds such as mercaptans, sulfides and cyclic sulfur-containing compounds.

SIGNIFICANCE

Sulfur can contaminate catalysts and cause corrosion in upgraders. Therefore, extensive sulfur removal procedures must be employed so that synthetic crudes meet refinery requirements. Emissions of sulfur oxides from refineries can contribute significantly to the acid-rain problem. Material balances for sulfur around a primary upgrading plant, which ensure adherence to environmental regulations, require an accurate measurement of the sulfur content of the feedstock.

Correlations between sulfur content and other properties of bitumen and heavy oil, which were developed for conventional crudes to identify their source, also apply to bitumen and heavy oil.[28] The vanadium-to-nickel atomic ratio increases and API gravity decreases with increasing sulfur content (Figures 6.1 and 6.2).

1. ASTM D1552: Sulfur in Petroleum Products (High Temperature Method)

1.1 Application

This method covers the determination of total sulfur in petroleum products boiling above 177°C and containing greater than 0.06% sulfur. The method is commonly referred to as the LECO-combustion method.

1.2 Summary of the Method

A test sample weighing up to 200 mg is burned in either a resistance or induction-type furnace to produce SO_2. The SO_2 is passed into an absorber containing an acid solution of potassium iodide and starch indicator where it reduces iodine by the reation:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + HI.$$

The iodate-iodide reaction which regenerates the iodine is

$$KIO_3 + 5KI + 6HCl \rightarrow 3I_2 + 6KCl + 3H_2O$$

The amount of potassium iodate required to liberate iodine and maintain a slight blue color in the absorber is a measure of the sulfur content of the sample.

Nitrogen in excess of 0.1% in the test sample can introduce a significant negative error into the sulfur determination because nitrous oxides react with potassium iodide to release elemental iodine. Under these conditions less potassium iodate will be required to maintain the indicator color. To eliminate this interference, sodium azide is added to the absorber solution where it reacts with NO by

$$4NaN_3 + 2NO + 2H_2O \rightarrow 4NaOH + 7N_2.$$

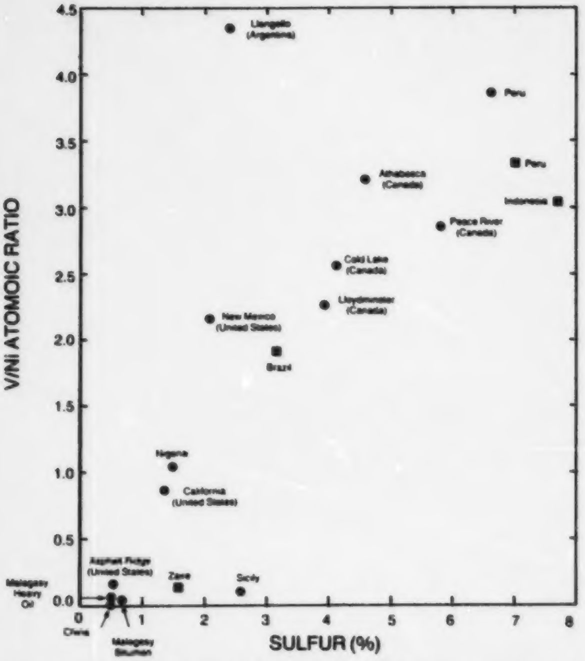

Figure 6.1: **Relationship Between Sulfur Content and V/Ni Atomic Ratio for a Variety of Bitumens and Heavy Oils.**[28] Squares denote samples which were severely weathered before sampling.

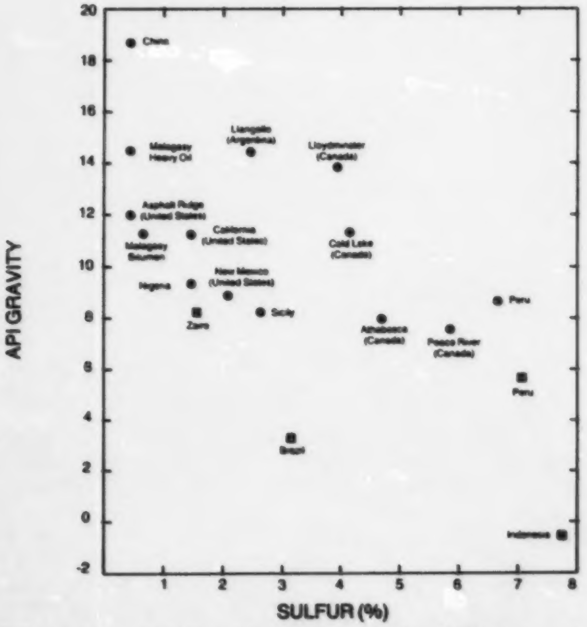

Figure 6.2: **Relationship Between Sulfur Content and API Gravity for a Variety of Bitumens and Heavy Oils.**[28] Squares denote samples which were severely weathered before sampling.

Not all sulfur in the sample is converted to SO_2. During rapid combustion in the LECO furnace the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ takes place to the extent that only about 97% of the sulfur remains in the form of SO_2. Therefore, a standardization factor for the equipment and reagents must be determined when conducting a set of analyses. The factor is calculated by burning a standard potassium alum, which is available from LECO, as described above. National Bureau of Standards SRM 1620, sulfur in residual fuel oil (4.48% S), and SRM 1622b, sulfur in residual fuel oil (1.98% S) are also used in some laboratories to determine the standardization factor.

1.3 Precision

Sulfur (%)	**Repeatability (%)**	**Reproducibility (%)**
ASTM		
<0.5	0.05	0.08
0.5-1.0	0.07	0.11
1.0-2.0	0.10	0.19
2.0-3.0	0.16	0.26
3.0-4.0	0.22	0.40
4.0-5.0	0.24	0.54
ACOSA[a]		
Lloydminster heavy oil	0.16	1.41
Athabasca bitumen	0.22	1.93
Phillips[b]	0.05	0.59
Wallace[c]	0.31	-
Herman[d]	8.8% relative	-

[a] Precision was determined from triplicate analysis by six laboratories of an Athabasca bitumen containing 4.9% sulfur and a Lloydminster heavy oil containing 4.0% sulfur.

[b] Precision was determined from duplicate analysis by three laboratories of a California heavy oil blend containing 3.5% sulfur and a Maya crude containing 3.3% sulfur.

[c] Precision was determined from duplicate measurements conducted on 32 samples of Athabasca bitumen containing approximately 4.7% sulfur.[29]

[d] Calculated from the data in Table 6.4.

2. ASTM D2622: Sulfur in Petroleum Products (X-ray Spectrographic Method)

2.1 Application

This method is applicable for the determination of total sulfur in liquid petroleum products that can be liquefied with moderate heating or dissolved in a white oil. The material tested may contain up to 5% sulfur after dilution.

2.2 Summary of the Method

The test sample is placed in an X-ray beam and the intensity of the sulfur Kα line at 5.373 Å is measured and subtracted from the intensity of the background at 5.190 Å. The concentration of sulfur is determined by comparing the net count with calibration curves prepared from certified standards (di-n-butyl sulfide) dissolved in white oil which contains less than five mg/kg of sulfur.

The standards used to prepare the calibration curve must be matrix-matched to the sample. Carbon-to-hydrogen ratios must therefore be similar for the samples and standards. Other elements which can interfere (P, Zn, Ba, Pb, Ca and Cl) are generally not found in bitumen above the maximum tolerable levels.

2.3 Precision

Sulfur (%)	Repeatability (%)	Reproducibility (%)
ASTM		
0.001 to 0.005	0.60 × %S	0.60 × %S
0.005 to 0.015	0.20 × %S	0.40 × %S
0.150 to 5.0	0.05 × %S	0.16 × %S
ACOSA[a]		
Athabasca bitumen	0.40	1.79
Lloydminster heavy oil	0.28	1.76
Phillips[b]	0.08	0.26

[a] Precision was determined from triplicate analysis by three laboratories of the Athabasca bitumen and Lloydminster heavy oil samples described in Section 1.3.

[b] Precision was determined from duplicate analyses by four laboratories of the California heavy oil and the Maya crude described in Section 1.3. These results include data from both dispersive (ASTM D2622) and non-dispersive (IP 336) methods.[20]

3. IP 336: Sulfur in Petroleum Products by Non-Dispersive X-ray Fluorescence

3.1 Application

This method describes the measurement of sulfur in hydrocarbons in the concentration range of 0.01 to 5% by weight.

3.2 Summary of the Method

This method is non-dispersive (a filter is used to remove unwanted fluorescence X-radiation) as opposed to ASTM D2622 in which a crystal is used to disperse the fluorescence X-rays and isolate the sulfur Kα line. The sample is placed in a beam emitted from an Fe-55 source. The resultant radiation is measured and compared to a calibration curve of di-n-butyl sulfide in white oil.

3.3 Precision

	Repeatability	Reproducibility
Institute of Petroleum	0.017 (%S + 0.8)	0.005 (%S + 0.8)
Frechette[a]	10% relative	

[a] Repeatability was determined from triplicate analyses of 31 petroleum products with sulfur content ranging from 0.01 to 2.68%.[8]

4. ASTM D3120: Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry and Syncrude Analytical Method 5.9: Determination of Sulfur in Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

4.1 Application

This method covers the determination of sulfur in liquid hydrocarbons with a final boiling point below 274°C and at levels between 3 and 100 mg/kg. For samples with higher sulfur contents, the method can be used providing the sample is diluted appropriately.

4.2 Summary of the Method

A test sample of bitumen or heavy crude is diluted in a sulfur-free solvent to obtain a solution of 3 to 100 mg/kg of sulfur. A 10-μL aliquot is injected at a rate of 0.1 to 0.2 μL/sec into a pyrolysis tube so that the sulfur is converted to SO_2. The SO_2 flows into a titration vessel where it reacts with tri-iodide by the reaction:

$$SO_2 + I_3^- + H_2O \rightarrow SO_3 + 3I^- + 2H^+.$$

The tri-iodide ion consumed in this reaction is generated coulometrically by

$$3I^- \rightarrow I_3^- + 2e^-$$

The number of microcoulombs required to regenerate tri-iodide is a measure of the SO_2 entering the cell and therefore the level of sulfur in the original sample.

During combustion, some of the sulfur is converted directly to SO_3 and so does not enter into the reaction. Therefore the system requires calibration with a reference material such as n-butyl sulfide diluted in iso-octane. Nitrogen, halides and heavy metals are not usually found in heavy crudes in concentrations that will interfere with this method.

4.3 Precision

The following statements were determined from the analysis of light liquid hydrocarbons with sulfur levels below 100 mg/kg.

Repeatability (% Relative)	Reproducibility (% Relative)
28	38

5. ASTM E443: Sulfur in Organic Compounds by Oxygen Flask Combustion (Schöniger Combustion)

5.1 Application

This method covers the determination of sulfur in samples ranging in sulfur content from 0.05 to 5% for materials ranging from gasolines to solids.

5.2 Summary of the Method

A test sample weighing up to 0.1 g is wrapped in filter paper and burned in an oxygen atmosphere in a combustion flask containing a solution of hydrogen peroxide. The sulfur gases produced during combustion are converted by the peroxide to sulfate which is then measured by barium chloride titration using Sulfanazo III to indicate the endpoint.

5.3 Precision

The ASTM precision statements are based on analyses of S-benzyl-thiouronium chloride, sulfonal and sulfonic acid.

	Repeatability (% Relative)	**Reproducibility (% Relative)**
ASTM	1.34	3.82
Wallace[a]	0.43	

[a] Repeatability was determined from duplicate determinations of sulfur in twenty-four samples of Athabasca bitumen containing approximately 4.8% sulfur.

6. IP 243: Sulfur in Petroleum Products: Wickbold Oxy-Hydrogen Method

6.1 Application

This method describes the determination of total sulfur in petroleum products with sulfur contents below 300 mg/kg. Heavy crudes and residues which are very viscous or have high sulfur levels are diluted before combustion.

6.2 Summary of the Method

A test sample is burned in a Wickbold combustion apparatus to produce sulfur dioxide which is converted to sulfate in a hydrogen peroxide solution. The sulfate is measured by barium perchlorate titration to a thorin endpoint. Interferences from metals exist (see IP242).

6.3 Precision

Repeatability	**Reproducibility**
$0.074\ (\%S)^{0.85}$	$0.24\ (\%S)^{0.85}$

7. IP 242: Sulfur in Petroleum Products: Flask Combustion Method

7.1 Application

This method covers the determination of total sulfur in petroleum products containing greater than 2% sulfur, including gas oils, fuel oils, residues, some lubricating oils, and some crudes.

7.2 Summary of the Method

A test sample weighing up to 30 mg is enclosed in filter paper and burned in an oxygen-rich atmosphere in a combustion flask containing a hydrogen peroxide solution. The sulfur gases are converted to sulfate in the solution and titrated with barium perchlorate to a thorin indicator endpoint.

Many metals found in bitumen or entrained solids (Na, K, Mg) may interfere in the titration but critical levels are not specified in the standard.

7.3 Precision

	Repeatability	**Reproducibility**
IP-Photometric Detection	0.04%	0.09%
Herman[a]	8.9% relative	-

[a] Calculated from the data in Table 6.4.

8. ASTM D129: Sulfur in Petroleum Products (General Bomb Method) and IP 61: Sulfur in Petroleum Products by the Bomb Method

8.1 Application

The method is applicable to petroleum products containing at least 0.1% sulfur and sufficiently low in volatiles to permit accurate weighing in an open boat.

8.2 Summary of the Method

A 0.3- to 0.8-g sample is oxidized in a bomb by combustion under pressure. Sulfur is precipitated as $BaSO_4$ from the oxygen bomb washings. The precipitate is filtered, ashed and weighed. If the original sample contains acid-insoluble materials such as silica, mica, iron, calcium, or aluminum compounds, erroneously high data will be reported.

8.3 Precision

The following precision statements were generated for a variety of petroleum products such as lube oils and greases, but probably did not include bitumen.

Sulfur (%)	**Repeatability (%)**	**Reproducibility (%)**
ASTM		
0.1-0.5	0.04	0.05
0.5-1.0	0.06	0.09
1.0-1.5	0.08	0.15
1.5-2.0	0.12	0.25
2.0-5.0	0.18	0.27
IP	0.016 (%S)+0.06	0.037 (%S)+0.13

9. ASTM D3177: Total Sulfur in the Analysis Sample of Coal and Coke (Eschka Method)

9.1 Application

Although designed specifically for the measurement of sulfur in coal and coke, this method is occasionally used for the analysis of bitumens and heavy oils.

9.2 Summary of the Method

A 1-g sample of bitumen is mixed in a crucible with 3 to 4 g of Eschka mixture (2:1 MgO: Na_2CO_3) and ignited. The residue is dissolved in dilute HCl. The sulfur is precipitated as $BaSO_4$, filtered, ashed, and weighed. Acid-insoluble materials such as those described in the previous method can contribute to high results.

9.3 Precision

Precision statements have been generated for the determination of sulfur in coal and coke but not in heavy crudes. For coal and coke, these statements are:

	Repeatability (%)	Reproducibility (%)
Coal <2% sulfur	0.05	0.10
Coal >2% sulfur	0.10	0.20
Coke	0.03	0.05

DISCUSSION

Nonstandard Methods for the Determination of Sulfur

In addition to the nine standard methods described previously for the determination of sulfur, numerous variations have been reported in the literature. Most employ combustion procedures as described in the standards and vary only in the measurement of the sulfur species. These variations include:

- measurement of the conductivity of the sulfate-containing solution and comparison to standard curves[9] with a Dohrmann 701 analyzer
- amperometric titration with a Fisher analyzer[20]
- polarographic determinations of either excess barium after addition of barium perchlorate[22] or excess chromate after addition of barium dichromate to precipitate the sulfate[2]
- use of a gas-sensing electrode to measure the SO_2 absorbed in a tetrachloromercurate solution[14]
- ion chromatographic determination of sulfate[16,17,23]
- conversion of SO_2 to SO_3 by, and adsorption on vanadium pentoxide followed by gravimetric determination of the adsorbed SO_3
- measurement of SO_2 by IR detectors[26] used in modern LECO analyzers
- measurement of sulfur by inductively-coupled plasma and atomic absorption spectroscopy[30]
- adsorption of sulfur oxides on copper oxide to form copper sulfate followed by heating to release SO_2 which is titrated coulometrically[19]
- reduction of sulfur to H_2S followed by photometric determination on a strip of paper impregnated with lead acetate[6]
- molecular emission cavity analysis[7]

These methods will not be reviewed further unless data from them are compared to data from ASTM or IP standard methods.

Comparison of Analytical Methods

More laboratories measured sulfur content than any other property for the samples distributed in the ACOSA and the Phillips cooperative studies. In the ACOSA study, a total of eight methods were used by the twenty-three participants. Seven methods were represented in the Phillips study in which twenty labs conducted determinations of sulfur. Because such a variety of methods was used, the only between-method comparison that could be made was for LECO and X-ray fluorescence data. The data provided in Table 6.1 show excellent agreement between these methods.

Researchers at the Alberta Research Council and the University of Alberta compared values for sulfur determined by the LECO (ASTM D1552) and Schöniger (ASTM E443) methods (Table 6.2). The differences between the two results were less than the reproducibility of ASTM D1552 for all samples containing less than 5% sulfur. The Indonesian bitumens contained crystals of elemental sulfur thereby contributing to the high sulfur contents and perhaps increased variability within the extracted samples of bitumen.

Table 6.1: Comparison of LECO and X-ray Fluorescence Sulfur Determinations from Cooperative Studies Both dispersive and non-dispersive X-ray methods are included.

	LECO		X-ray	
	Number of labs	Sulfur (%)	Number of labs	Sulfur (%)
ACOSA				
Athabasca bitumen	6	4.89	4	4.81
Lloydminster heavy oil	6	4.01	4	4.00
Phillips[20]				
California heavy oil	3	3.45	4	3.47
Maya crude	3	3.31	4	3.30

Table 6.2: Comparison of Data from LECO and Schöniger Determinations of the Sulfur Content of Bitumen

	Sulfur (%)		
	ASTM D1552	ASTM E443	Discrepancy from ASTM D1552 (% Relative)
Malagasy	0.48	0.45	− 6.3
Lloydminster	4.39	4.10	− 6.6
Argentina	2.43	2.52	+ 3.7
Indonesia	6.38	7.59	+18.9
Indonesia	16.60	17.14	+ 3.3
Wabasca	3.93	3.73	− 5.0
Athabasca	4.70	4.60	− 2.1
Cold Lake	4.65	4.45	+ 4.3
Diluted Athabasca bitumen	2.90	2.96	+ 2.1

The data are described by the line

$y = 0.95x + 0.17$

where y = the ASTM D1552 values and

x = the ASTM E443 values

Standard deviations: Slope: 0.03

Intercept: 0.22

In his paper describing ion chromatography as a technique for measuring the amount of sulfur in fuel oils, McCormick provided comparisons with molecular emission cavity analysis, X-ray fluorescence and titration of $SO_4^=$ with barium to a thorin endpoint as described in IP 242.[16] His comparisons are given in Table 6.3.

Herman and Kochanowska compared sulfur determinations using a LECO DB-64 sulfur analyzer with an automatic titrator (ASTM D1552), a Schöniger combustion followed by titration to a thorin endpoint (IP 242) and a calorimetric bomb method with a gravimetric determination of barium sulfate (similar to ASTM D129 but registered in Poland as DN-62/C-04091).[10] The results are provided in Table 6.4. All methods gave equivalent results. Herman and Kochanowska reported that in the LECO analyzer, water can condense in the system and dissolve SO_2 before it reaches the titration unit, thereby causing low results for sulfur.

Frechette and co-workers found good agreement between X-ray fluorescence and ASTM D1552 for refinery samples ranging from 0.01 to 2.7% sulfur[8] (Table 6.5).

Table 6.3: Results for the Determination of Sulfur Content of Oils Using Different Methods (Reprinted with permission from Anal. Chim. Acta. 1980, 121, 233-238.)

		Sulphur (%)			
Sample	Description of oil	X.R.F.[b]	Titration	Ion chromatography[a]	M.E.C.A.[a]
NBS Standard 1621 % S = 1.05 ± 0.02	Heavy residual fuel oil	1.06	1.05 ± 0.03	0.99 ± 0.03[c]	0.9 ± 0.1[c]
NBS Standard 1623 % S = 0.268 ± 0.004	Light distillate fuel oil	0.27	0.29 ± 0.05	0.265 ± 0.004	0.26 ± 0.02
NBS Standard 1634 % S = 2.14 ; 0.02	Heavy fuel oil with small amount of residue	2.17	2.0 ± 0.1	2.154 ± 0.009	2.0 ± 0.2
1	Heavy fuel oil with no residue stock	2.67	2.845 ± 0.006	2.60 ± 0.03	2.13 ± 0.02
2	Diesel oil C11-C25	0.10	0.19 ± 0.02	0.08 ± 0.01	0.087 ± 0.004[d]
3	Industrial diesel oil C11-C30	0.26	0.16 ± 0.01	0.24 ± 0.01	0.18 ± 0.09[d]
4	Blended oil containing kerosene to lower viscosity	2.86	2.50 ± 0.04	2.78 ± 0.02	2.5 ± 0.2
5	Diesel oil C10-C25	0.10	0.16 ± 0.10	0.101 ± 0.009	0.096 ± 0.001[d]

[a] Based on triplicate analyses unless otherwise stated; mean ± standard deviation.

[b] Based on single analyses.

[c] Based on six replicate analyses.

[d] Based on duplicate analyses.

X-ray Fluorescence

With the exception of the technique used to isolate the X-radiation, dispersive and non-dispersive X-ray methods are so similar that they can be considered as one for sulfur determinations. The equipment used for dispersive X-ray (Phillips spectrometers, for example) is much more complex and expensive but it permits the determination of many other elements in the sample. Non-dispersive spectrometers (Horiba, for example) are a fraction of the cost but are dedicated to sulfur determinations alone.

The major problem with an X-ray fluorescence determination of sulfur in oils is the variation between matrices in absorption of both the primary X-rays and the fluorescence X-rays. Carbon and hydrogen mass absorption coefficients are 198.81 and 2.54 for sulfur Kα radiation.[4] Therefore, the total absorption coefficient of crude oils is highly dependent on both the concentrations of carbon and hydrogen in the sample and their ratios. This coefficent will determine the slope of the calibration curve. Ishii and Fujiwara showed that when standards were prepared in a matrix with a carbon-to-hydrogen mass ratio of 7.5, X-ray fluorescence seriously underestimated the sulfur content in samples with a carbon-to-hydrogen ratio above 9.[12]

The problem of matrix effects can be eliminated by preparing a calibration curve with standards of the same matrix as the sample to be analyzed, if the matrix is known. Horiba has supplied the recipes for preparing

Table 6.4: Comparison of Sulfur Determinations for Petroleum Products (Reprinted with permission from Nafta 1980, 2, 61-64.)

	Sulfur (%)					
	Calorimetric bomb		IP 242		ASTM D1552	
		$\bar{x}$		$\bar{x}$		$\bar{x}$
Kerosene from	0.20		Below detection		0.155	
Kirkuk crude	0.16	0.18	limit		0.147	0.15
	0.17				0.156	
Raffinate from	0.52	0.51	0.57		0.561	
Kirkuk crude	0.50		0.57	0.55	0.580	0.56
			0.52		0.553	
Heating oil	1.18		1.08		1.09	
	1.24	1.21	1.08	1.10	1.21	1.13
			1.15		1.10	
Fuel from catalytic	2.04		2.03		2.09	
cracker	1.99	2.02	2.00	2.03	2.10	2.05
			2.06		1.96	
de-parrafinate	2.10		1.99		2.13	
	2.09	2.10	2.00	2.04	2.11	2.14
	2.20		2.12		2.18	
Kirkuk crude blend	1.91		2.24		2.30	
	2.07	2.08	2.25	2.22	2.30	2.31
	2.26		2.17		2.34	
360°C + residue	3.56		3.67		3.64	
from Kirkurk crude	3.49	3.54	3.52	3.56	3.58	3.61
	3.58		3.51		3.60	
Furfurol extract	5.06		5.14		5.20	
	5.07	5.07	5.24	5.15	5.19	5.21
	5.07		5.06		5.23	
Repeatability	16.7		8.9		8.8	
(% Relative)	(11.6 excluding kerosene data)					

Table 6.5: Comparison of Sulfur Determinations in Distillate and Residual Fuel Oils[a]

	Sulfur (%)			
	ASTM D1552 (Referee lab)	ASTM D1552 (Golden Eagle refinery)		ARL Non-dispersive X-ray (Integration time: one minute) (Golden Eagle refinery)
		Manual	Automatic	Mean[e]
Stove oil				
1	(0.02)[a]	(0.019)[3]		(0.022)[d]
2	(0.13)[b]	0.126	0.122	0.132
3	(0.011)[c]	(0.010)[c]	(0.008)[c]	(0.013)[d]
4	0.31	0.29	0.33	0.320
5	0.14	0.151		0.132
6		(0.090)[c]		(0.089)[d]
7		0.21	0.20	0.231
Furnace oil				
1	0.23	0.21	0.25	0.232
2	0.35	0.385	0.333	0.379
3	0.27	0.23	0.24	0.226
4	0.36	0.37	0.35	0.343
5	0.27	0.28	0.30	0.267
6		0.33	0.35	0.393
7		0.38	0.38	0.408
Diesel fuel				
1	0.12	0.113	0.106	0.121
2	0.32	0.353	0.285	0.343
3	0.30	0.25	0.23	0.265
4	0.70	0.68	0.72	0.733
5	0.21	0.20	0.22	0.210
6		0.48	0.49	0.516
7		0.38	0.45	0.406
Bunker C				
1	2.74	2.71	2.69	2.68
2	2.58	2.56	2.60	2.62
3	1.33	1.36	1.31	1.39
4	2.35	2.41	2.30	2.33
5	2.14	2.30	2.42	2.19
6		2.01	2.10	2.00
7		2.60	2.52	2.49
100ppmV, 12ppmNi	0.64	0.63	0.64	0.66
200ppmV, 25ppmNi	1.40	1.44	1.36	1.41
300ppmV, 37ppmNi	2.13	2.05	2.20	2.06

[a] ASTM D2785 Trace Quantities of Total Sulfur: Wickbold and Beckmann Combustion Apparatus (time per analysis: 90 minutes).

[b] ASTM D1266 Lamp Method (time per analysis: 2-6 hours).

[c] Raney Nickel Sulfur Method (time per analysis: 2 hours).

[d] ARL Non-Dispersive X-ray Analyzer N-900 (integration time: 2 minutes).

[e] Mean of three determinations.

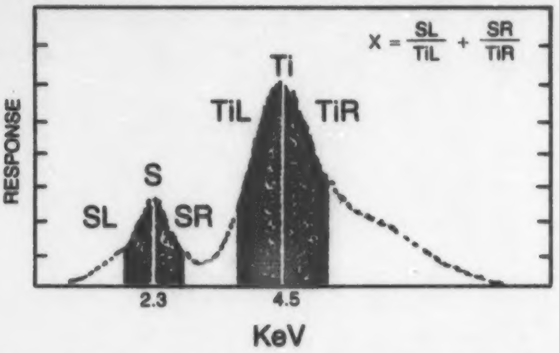

Figure 6.3: **Typical Spectrum used to Correct Sulfur for Matrix Effects** (Reprinted with permission from Am. Lab. 1983, 15(11), 27-42. Copyright 1983 by International Scientific Communications, Inc.)

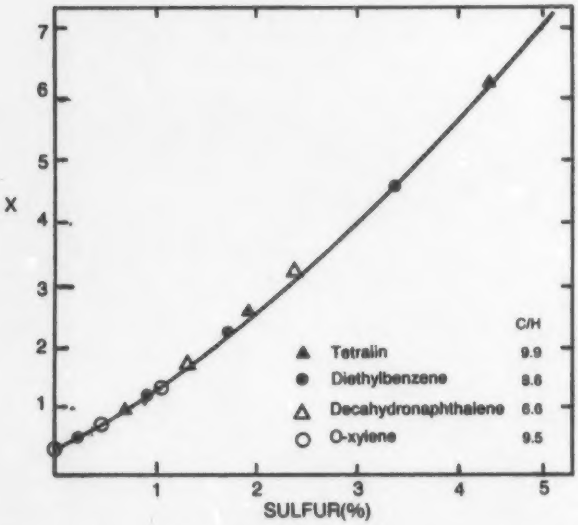

Figure 6.4: **Calibration Curve Corrected for Matrix Effects for Sulfur in Different Matrices** (Reprinted with permission from Am. Lab. 1983, 15(11), 27-42. Copyright 1983 by International Scientific Communications, Inc.)

standards of varying sulfur concentrations and carbon-to-hydrogen ratios.[11] Alternatively, the method of standard addition can be used. Yousif and Al-Shahristani added known amounts of CS_2 to crude oil and extrapolated to the initial sulfur concentration.[33] Akama and co-workers at Meisei University in Japan[1] and Bauer and co-workers at the British Railways Technical Centre in the United Kingdom[3] solved the matrix problem by making a pellet of the sample and standards in paraffin wax. Presumably, the paraffin wax matrix would tend to override any differences in the carbon-to-hydrogen ratios in the samples and standards.

Other solutions to the matrix effect problem are mathematical in nature. Some involve complex theoretical calculations and large amounts of data to make corrections.[5,13] Takahashi and Rey described a simpler empirical approach to matrix correction which is employed by the Dohrmann 702 sulfur analyzer.[25] They assumed that the fluorescent sulfur line from the sample and the scattered titanium line from the X-ray source are both absorbed to a similar degree by the matrix as their energies are similar. They fixed two windows on each side of the sulfur peak and two on each side of the titanium peak (Figure 6.3). They then summed the ratios of SL/TiL and SR/TiR and established a second degree polynomial calibration curve of this sum (*X*) against sulfur content (%S) in the standards. The value *X* is fairly independent of matrix type (Figure 6.4) and so a matrix-free calibration curve is established. The method of ratios also eliminates the contribution of variations in primary beam intensity due to system instability. A change in the counts in the sulfur windows would be cancelled by a similar change in the counts in the titanium windows. With this procedure, Takahashi and Rey found good correlations when they compared the Dohrmann X-ray results to microcoulometric determinations for a variety of standard and refinery samples (Tables 6.6 and 6.7).

Additional error in the X-ray methods arises from the fact that the sulfur Kα line has a relatively low intensity and can penetrate only a thin film of oil. Figure 6.5, provided by Yousif and Al-Shahristani, suggests a depth of 0.5 mm is required to ensure that the sulfur counts are independent of film thickness.[33] Takahashi and Rey found that gross sulfur counts were dependent on depth up to a thickness of 10 mm (Figure 6.6).[25] Bauer and co-workers used paraffin pellets only 0.1 mm thick.[3]

Table 6.6: **Comparison of Non-Dispersive X-ray Fluorescence and Microcoulometry (ASTM D3120)** (Reprinted with permission from Am. Lab. 1983, 15(11), 27-42. Copyright 1983 by International Scientific Communications, Inc.)

	Sulfur (%)		
Matrix	**Nominal**	**ASTM D3120**	**XRF**
Res. fuel oil (NBS 1622B)[a]	1.982	1.977	1.979
Res. fuel oil (NBS 1621B)	0.950	0.935	0.944
Res. fuel oil (NBS 1623A)[a]	0.240	0.230	0.238
Dist. fuel oil (NBS 1624A)	0.141	0.140	0.145
Lube oil (Alpha Resources)[a]	0.67	0.671	0.672
	0.48	0.460	0.477
	0.082	0.091	0.086
Kerosene (Alpha Resources)	0.51	0.500	0.510
	0.069	0.083	0.074
	0.048	0.056	0.052
Paraffin oil blank[a]	0.0	0.0005	0.005

[a] Calibration standards.

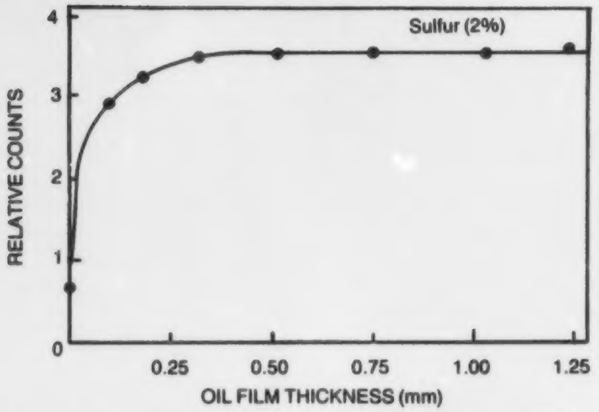

Figure 6.5: **Variation in Sulfur Kα Count Rate with Oil Film Thickness** (Reprinted with permission from Int. J. Appl. Rad. Isot. 1977, 28, 759-763.)

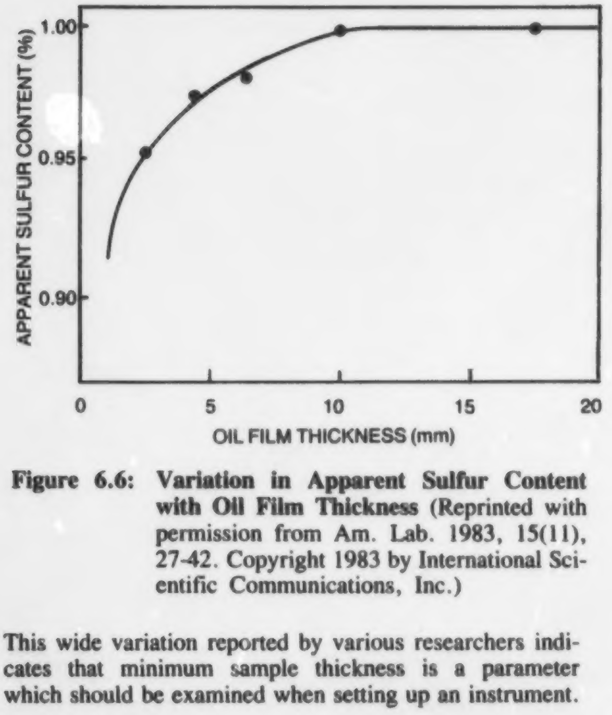

Figure 6.6: **Variation in Apparent Sulfur Content with Oil Film Thickness** (Reprinted with permission from Am. Lab. 1983, 15(11), 27-42. Copyright 1983 by International Scientific Communications, Inc.)

This wide variation reported by various researchers indicates that minimum sample thickness is a parameter which should be examined when setting up an instrument.

In the Princeton Gamma Tech and Horiba analyzers the sample is held in a plastic cup and in contact with a plastic film. If the sample is light enough or is an emulsion, some polar sulfur-containing species may preferentially move to the film and result in an enrichment of the surface in terms of sulfur content compared to the bulk. It is good practice to ensure that the elapsed time between analysis and initial placement in sample cells is the same for both standards and samples. Reference standards should not be stored for extended periods as the apparent sulfur content will change with time.

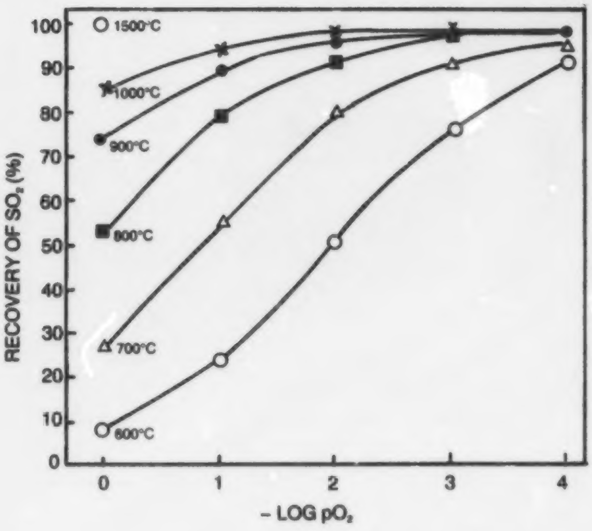

Figure 6.7: **Effect of Temperature and Partial Pressure of Oxygen on SO_2 - SO_3 Equilibrium** (Reprinted with permission from Anal. Chem. 1977, 49, 1615-1618. Copyright 1977, American Chemical Society.)

Tabati and Matsumoto examined yet a different type of matrix effect — that caused by the presence of water in a sample.[24] They prepared dispersions of water and waste oils from gasoline engines and found that the measured sulfur content varied with both water content and age of the dispersion. They attributed the "aging" effect to water breaking out of the sample and reflecting both the incident primary radiation so it does not reach the oil, and the fluorescent radiation so it does not reach the target. They recommended that all samples containing in excess of 3% water should be dried before analysis. Although water-in-bitumen emulsions are probably more stable than the dispersions studied here, the "mirror" effect could cause a significant bias in the data unless a ratio correction as described earlier is used.

Oxidative Microcoulometry

Oxidative and reductive microcoulometric methods can both be used for the determination of sulfur in hydrocarbons. In the former method, sulfur is oxidized to SO_2 which is titrated with I_3^-. In the latter, sulfur is converted to H_2S which is titrated with Ag^+. The oxidative method is simpler to operate and is recommended when the concentration of heavy metals, nitrogen or chlorine is not excessive. However, some of the sulfur is converted to SO_3 during combustion and corrections must be employed. On the other hand, the reductive method does not suffer from heavy metal or chlorine interference although nitrogen will introduce a positive error to the sulfur determination.[31]

Table 6.7: Comparison of Non-Dispersive XRF and ASTM D3120 for Refinery Samples (Reprinted with permission from Am. Lab. 1983, 15(11), 27-42. Copyright 1983 by International Scientific Communications, Inc.)

	Sulfur (%)	
	ASTM D3120	XRF
Gas oil	1.490	1.497
Diesel fuel prod.	0.257	0.251
Hydrotreater feed	0.361	0.376
Neutral lube oil	0.064	0.072
Jet fuel	0.029	0.026
Synthetic gas oil	0.392	0.391
Oil #1	0.119	0.117
Fuel oil[a]	0.240	0.247

[a] Containing 0.049% Cl.

The major concerns in oxidative microcoulometry do not lie in the adsorption of SO_2 and titration, but rather in the mechanics of injecting the test sample into the pyrolysis-combustion chamber and variations in the equilibrium between SO_2 and SO_3. SO_3 produced during combustion is not titrated, resulting in low estimates of sulfur. Consideration of the equilibria involved in the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$ shows that a high sulfur dioxide yield is favored by high temperature and low partial pressure.[32] Figure 6.7 illustrates the relationship between SO_2 yield and these two combustion conditions. At 1 atmospheric pressure of oxygen ($-\log pO_2 = 0$), an increase in combustion temperature from 800 to 1500°C results in an increase in yield of SO_2 from 52 to 100%.

Combustion conditions commonly employ pyrolysis and vaporization under an inert gas at temperatures up to 700°C followed by oxidation at 800 to 1000°C. In the oxidation zone, the oxygen to inert gas ratio is 4:1. Under these conditions the conversion to SO_2 should exceed 75%. However, heavy materials may be incompletely oxidized resulting in the formation of a sulfur-bearing carbonaceous deposit around the oxidation furnace, leading to low estimates of sulfur content. On the other hand, these conditions can lead to the formation of other species such as olefins and aldehydes which react with iodine in the titration cell and are measured as sulfur.

To overcome these problems, White injected samples directly into an oxygen-rich combustion chamber at 700°C so that no coke was formed.[32] Combustion gases were diluted with helium to minimize conversion to SO_3. He reported conversions to SO_2 of 98 to 99% for a variety of sulfur compounds, which was a significant improvement over the lower (85%) and more variable (±5%) recovery using standard procedures.

Table 6.8: Comparison of LECO and Oxidative Microcoulometry Sulfur Data for Heavy Petroleum Products (Reprinted with permission from Anal. Chem. 1980, 52, 760-765. Copyright 1980, American Chemical Society.)

	Sulfur (%)	
	LECO	Oxidative Microcoulometry[a]
Ekofisk crude	0.24	0.23
Sun finished crude	0.32	0.32[b]
Texoma crude	0.39	0.38
Peruvian crude	0.48	0.47
Cat. cracker chg.	0.52	0.49
Crude vac. bottoms	0.96	0.94
Slurry oil	1.64	1.64

[a] Diluted in toluene to 20 ppm sulfur.

[b] Measured 0.31% against thiophene.

White also found that dilution of heavy materials so that they can be injected by syringe can lead to low values for sulfur because the diluent tends to evaporate from the needle and leave an involatile residue (some of the test sample) behind. To overcome this problem he recommended use of a diluent containing no sulfur but with a boiling range as close to the test sample as possible. Wallace and co-workers found that if the sample is injected into a quartz boat in a hydrogen atmosphere and the boat is slowly pushed into an 800°C inlet, better accuracy and precision result.[31]

Moore and co-workers further refined the combustion cycle for heavy residues.[18] They injected samples onto a platinum boat in an inert atmosphere. The boat was inserted rapidly into an 800°C region where pyrolysis occured. The pyrolysis gases were carried to a combustion zone to produce SO_2 which was titrated automatically. After 45 seconds, oxygen was allowed to flow over the residue thereby burning it to ash and releasing the remaining SO_2. For lighter compounds, Moore eliminated the interferences due to chlorine and nitrogen by incorporating a tin-scrubber which reduced NO_x gases to NO and retained chlorine gases as $SnCl_2$. He also used an automated injection system to control the rate of injection (combustion) of the sample and improve precision. The cited reference indicates that attempts were underway to install the scrubber on a unit with a boat-inlet system but no results were reported. Conversions of sulfur to SO_2 of less than 60% efficiency indicated an unacceptably high accumulation of metals, which catalyze production of SO_3, in the pyrolysis tube. The metals were removed with 10% nitric acid. Moore found good agreement between sulfur data reported for crudes analyzed by ASTM D1552 and the boat-injector-microcoulometer system (Table 6.8).

Sampling Considerations

Elemental sulfur is sometimes produced from oxidation of pyrite which is found in trace quantities in Athabasca oil sand but has been found in levels above 1% in other deposits. The reaction is summarized by the equation[15]

$$20_2 + FeS_2 \rightarrow FeS_2(O_2) \rightarrow Fe^{2+} + S^{o} + SO_4^{2+}$$

Elemental sulfur is sufficiently soluble in hot toluene to be extracted from the oil sand with the bitumen and, if undetected in its crystalline form, will be measured as a component of the bitumen. Oxidation of pyrite can occur either in-situ if the formation is permeable to air and water or after sampling if the samples are not frozen. Elemental sulfur has been found in oil sand from Malagasy, Indonesia, Nigeria and Peru.[28] The Indonesian oil sand contained approximately 2.5% sulfur which raised the measured sulfur content of the test sample of bitumen from approximately 6 to 17%.

The variability of Athabasca bitumen between local sites as measured by sulfur content tends to be less than analytical variability. In two separate studies, Wallace and co-workers found the sampling standard deviation for 7-kg oil sand samples collected from a 45-gallon drum of oil sand was 0.05% or less.[27,29] Subsampling plus analytical uncertainty in both cases was in the range of 0.15%. Measurement of sulfur by X-ray fluorescence in Athabasca oil sand has been proposed as one means of quickly estimating the bitumen content.[21] This method is not routinely used because bitumen on the scale of a deposit is very heterogeneous with respect to sulfur content. In one lease in the Athabasca deposit, the sulfur content of the bitumen in one-foot core sections varied from 3.8 to 5.5%.[27]

SUMMARY

This review has identified nine standard methods and eleven nonstandard techniques that have been used for determining sulfur in petroleum products. Individual researchers have reported good agreement between many of the tests. In cooperative studies, so many methods have been employed that between-method comparisons are difficult to make. The studies have only served to show that for bitumens and heavy oils the average LECO data equal the average XRF data. However, the reproducibility of both of these methods in the studies was poorer than specified in the standards. Oxidative microcoulometry can be employed successfully by introducing oxygen into the injection port so that the sample is completely oxidized.

Due to the importance of sulfur measurements and the variety of methods available to an analyst, certified standards, specifically of bitumens and heavy oils, are required to reduce inter-laboratory errors.

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Chapter 7: AVERAGE MOLECULAR WEIGHT

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AVERAGE MOLECULAR WEIGHT

DEFINITION

The average molecular weight determined by a colligative property of bitumen in solution is a number-average molecular weight (M_n). To determine M_n, the number of molecules in a known mass of bitumen is estimated from thermodynamic relationships such as boiling point elevation, freezing point depression and osmotic pressure.

Size exclusion (gel permeation) chromatography can also provide a number-average molecular weight (M_n), and in addition provides a weight- or mass-average molecular weight (M_w) and a distribution of the sizes of the molecules in a sample. If a chromatogram of amount of sample eluted (*y*-axis) vs. time (*x*-axis) is divided into *z* equal slices along the *x*-axis:

$$M_n = \frac{\sum_{i=1}^{z} A_i}{\sum_{i=1}^{z} \frac{A_i}{M_i}} \quad \text{and} \quad M_w = \frac{\sum_{i=1}^{z} A_i M_i}{\sum_{i=1}^{z} A_i} \qquad (1),\ (2)$$

where A_i is the area of the *i*th slice and M_i is the average molecular weight of the components eluted in the ith slice as determined by a standard calibration curve.[10] The mass-average molecular weight is therefore a weighted average which considers the number of molecules of each molecular weight.

SIGNIFICANCE

In isolation, an average molecular weight tells very little about a bitumen or heavy oil. However, the average molecular weight of a whole bitumen provides a reference point for monitoring hydrocarbon upgrading processes, and is also used with ^{1}H-NMR and ^{13}C-NMR measurements to deduce average molecular structures[7], although controversy exists over the meaning and usefulness of an average structure.[1] In addition, the average molecular weights of petroleum fractions are used with API gravity to estimate heat capacities required in refinery processing.[2]

Speight and co-workers prepared a review of methods used to determine average molecular weights and the distribution of molecular sizes in asphaltenes.[22] These methods were osmometry, size exclusion chromatography, ultrafiltration, ultracentrifugation, and small-angle X-ray scattering. Size exclusion chromatography (SEC), vapor pressure osmometry (VPO) and freezing point depression (FPD), which are the three most commonly used methods, will be discussed here.

METHODS

1. Syncrude Analytical Method 5.6: Determination of Average Molecular Weight of Bitumen by Freezing Point Depression.

1.1 Application

This method determines the number-average molecular weight of bitumens, and other hydrocarbons with average molecular weights between 150 and 700 daltons (grams per mole).

1.2 Summary of the Method

The cooling curve for a 25-g sample of benzene weighed to the nearest 0.01 mg. is obtained using an insulated cooling container. The benzene is allowed to thaw and a 0.5-g test sample, weighed to the nearest 0.1 mg, is dissolved in it. The cooling curve for the solution is then obtained. The number-average molecular weight is determined from:

$$M_n = \frac{W(K_f - \Delta T)}{(\Delta T)\ (S)} \qquad (3)$$

where:

M_n = number-average molecular weight (daltons)
W = weight of sample (g)
K_f = cryoscopic constant for benzene (65.6)
S = moles of solvent
ΔT = freezing point depression (C°)
= freezing point of benzene - freezing point of solution

1.3 Precision

	Repeatability (% Relative)	Reproducibility (% Relative)
ASTM D2224[a]	5	—
ACOSA[b]	8	21
Guieze[c]	15	—

[a] Repeatability is quoted in this standard for mineral insulating oils.

[b] From triplicate analyses, by three laboratories, of an Athabasca bitumen (M_n = 460) and a Lloydminster heavy oil (M_n = 380).

[c] From a single analysis of two residues (M_n = 300) by nine analysts in one laboratory.[10]

2. UOP 676-71: Molecular Weight by Osmometry and ASTM D2503: Molecular Weight (Relative Molecular Mass) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure.

2.1 Application

These methods determine the number-average molecular weight petroleum and petroleum fractions with average molecular weights up to 3000 daltons and initial boiling points above 220°C.

2.2 Summary of the Methods

A vapor pressure osmometer is a conventional Wheatstone bridge with two thermistor probe beads in a closed chamber. The chamber is saturated with solvent vapor such as benzene, toluene or chloroform and a drop of that solvent is placed using a syringe on each thermistor. The bridge controls are adjusted until zero potential exists between the two samples. A drop of solution containing a known concentration of sample is then placed on one of the thermistors. Because the vapor pressure of the solution is lower than that of the pure solvent (Raoult's Law), solvent vapor condenses on the sample thermistor and causes a temperature difference between it and the thermistor with the pure solvent. The temperature difference, ΔT, is determined by measuring the voltage (V) between the thermistors. The net heat of condensation is a function of the molar concentration of the solute and is compared to calibrations using solutions of known molar concentrations of benzil in benzene.

In ASTM D2503, a calibration curve of the resistance, R, between the thermistors, which is proportional to V and ΔT, versus the molar concentration, (M) is prepared. The molar concentration of an unknown can be read directly from this curve. This method is appropriate whenever the solute molecules do not associate with one another.

Association of molecules, particularly asphaltenes, can be a problem when determining the average molecular weight of bitumens and heavy oils.[16,20,21,22] To overcome the concentration-dependence of a reading, the molecular weight is determined at an extrapolated concentration (C) of zero by plotting R/C vs. C for a series of calibration standards. A constant, K, is calculated from $K = M \times (R/C)_{C=0}$ where M is the molecular weight of the standard and $(R/C)_{C=0}$ is the y-intercept. Solutions containing the unknown fraction are prepared and their values are determined. Again, R/C vs. C is plotted and the y-intercept, A, is estimated by extrapolation. The average molecular weight, M_n, then equals K/A.

2.3 Precision

	Repeatability (daltons)	Reproducibility (daltons)
ASTM D2503[a]		
$245 < M_n < 399$	5	14
$400 < M_n < 599$	12	32
$600 < M_n < 800$	30	94
UOP 676 - 71		
$M_n = 375$	7	—
ACOSA[b]	17	45

[a] ASTM D2503 does not specify a solvent. These statements are based upon determinations in benzene. Precision using solvents such as toluene, chloroform and trichloroethane has not yet been established.

[b] From triplicate analyses by five laboratories of an Athabasca bitumen (M_n=530) and a Lloydminster heavy oil (M_n=480) using toluene as the solvent.

3. Size Exclusion (Gel Permeation) Chromatography

3.1 Application

Size exclusion chromatography (SEC), sometimes called gel permeation chromatography (GPC), has been developed for the determination of number-average and mass-average molecular weights and the distribution of molecular sizes in petroleum distillation residues. Petroleum component molar masses from 100 to 10,000 g/mol can be identified.

3.2 Summary of the Methods

Several SEC methods have been described for determining the molecular weights of asphalts,[1,19] asphaltenes,[11,18] bitumens,[4] pitches[11] and petroleum distillation residues.[10] In these methods, a solution of the sample is pumped through a column containing a porous chromatographic stationary phase. The larger molecules tend to be excluded from the pores and are eluted first. The smaller molecules enter the pores and take longer to pass through the column. Flame ionization or a combination of UV-IR detectors for detection of unsaturated and paraffinic compounds may be used to detect the sample. The sample's chromatogram is then compared to a chromatogram obtained from the separation of known compounds or petroleum fractions characterized by VPO or FPD.

3.3 Precision

A repeatability of 4% relative was calculated from Guieze's data in which a total of seven analyses of a residue were performed by three operators from one laboratory over a three-month period.[10]

DISCUSSION

Intermolecular Association in Colligative Property Methods

Many researchers have observed decreases in apparent molecular weight with increasing temperature, increasing solvent power and decreasing concentration of the sample in the solvent.[5,6,9,11,16,17,20,21,22] Examples of the effects of solvent power and concentration is given in Table 7.1. Although most molecular weight studies have been carried out on precipitated asphaltenes, these trends also apply to asphalts. They have not been reported as widely for bitumens and heavy oils. In early work, Moschopedis, Fryer, and Speight reported that the molecular weight of asphaltenes does not vary with asphaltene concentrations in benzene between 2 and 7%.[16] At the time of the study, vapor pressure osmometers were not sensitive enough to record temperature differences for solutions below 2%. Newer models routinely handle solutions of 0.1 wt% and as a result, association between molecules which were not evident earlier can now be identified (Figure 7.1). Therefore, newer osmometers using low solute concentrations may provide lower molecular weight values than those reported previously.

Table 7.1: Effect of Solute Concentration and Solvent Power on Number-Average Molecular Weight of Asphaltenes (Reprinted with permission from Revue de l'Institut Francais du Petrol 1985, 40, 51-61.)

Concentration (%)	M_n by VPO (daltons) in benzene 37°C	in pyridine 37°C
1.7	4850	
2.0		2655
3.0	6070	
3.3		2920
4.2	6440	
5.0		3480
7.0		4090

Also due to the safety hazards associated with benzene, many laboratories use toluene in their VPO measurements. As the solvent powers of benzene and toluene are similar, any difference in the molecular weights reported is probably a result of the higher temperature at which measurements are taken when toluene is used.

Although extrapolation to infinite dilution provides a means of reducing the effect of molecular association when determining average molecular weight, very few of the data in the literature have been obtained by this method. Figure 7.1 indicates that an extrapolated value from an instrument requiring a sample concentration of at least 1% will be considerably higher than an extrapolated value obtained from newer, more sensitive equipment. Therefore, extrapolation should be adopted as a standard practice in VPO measurements until it is proven to be unnecessary for a particular solvent. The temperature at which measurements are taken, the sample concentrations and the solvent used should be reported.

Comparison of VPO and FPD

Given the reported dependence of molecular weight on temperature and concentration, one would expect that molecular weights derived from freezing point depression would be higher than those from vapor pressure osmometry. For example, the freezing point of benzene lies near 5°C, while VPO measurements with benzene are typically taken at 35 to 60°C. Also FPD measurements require bitumen concentrations of 20 mg/mL, while VPO measurements are taken at concentrations between 0.1 and 7 mg/mL.

Despite these facts, FPD measurements usually yield lower results than VPO measurements (Table 7.2). There are two possible explanations. First, when FPD measurements are taken in benzene, it is difficult to prevent condensation of atmospheric moisture. The admission of moisture to a sample causes increasingly large errors with increasing molecular weight. To overcome this problem, phenanthrene (m.p. = 180°C) or camphor (m.p. = 100°C) may be used as cryoscopic solvents for high boiling point fractions.[15]

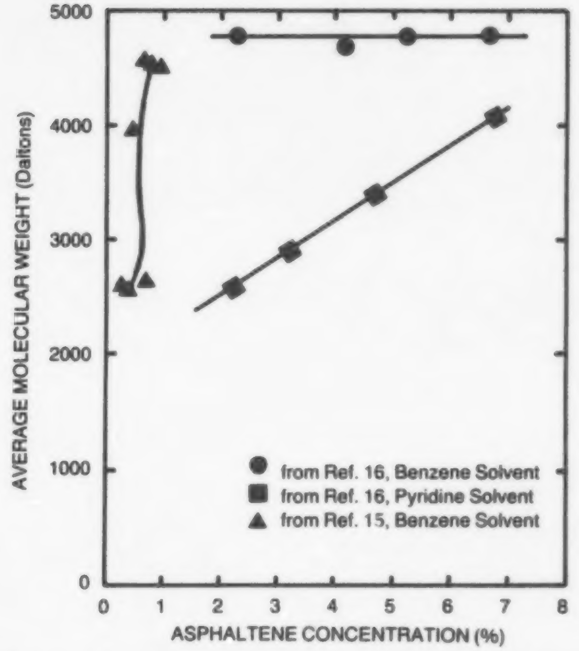

Figure 7.1: Effect of Asphaltene Concentration on Average Molecular Weight Measured by VPO

Table 7.2: Comparison of FPD and VPO for Determining Number-Average Molecular Weight[a]

	M_n (daltons)	
	FPD	VPO
Suncor coker feed bitumen	458[a]	531[b]
Lloydminster heavy oil	381[a]	487[b]
Solvent-extracted Athabasca bitumen[c]	551	605
Suncor coker feed bitumen[c]	462	607
Fireflood Athabasca bitumen[c]	286	319
Lloydminster heavy oil[c]	463	466

[a] Mean results from three laboratories using benzene as a solvent (ACOSA cooperative study).

[b] Mean results from nine laboratories using benzene, chloroform or toluene as solvents (ACOSA cooperative study).

[c] Alberta Research Council data; both FPD and VPO were carried out using benzene.

Table 7.3: Comparison of Experimental and Theoretical Number-Average Molecular Weights of Bitumen-Toluene Mixtures[12]

	M_n (daltons)	
Toluene (%)	Experimental	Theoretical[a]
0.00	574	574
0.27	522	566
0.66	562	555
1.87	554	523
5.20	574	451
8.88	546	392
9.76	579	380

[a] A sample calculation of the theoretical average molecular weight follows:

$M_{bit} = 574$ and $M_{tol} = 92.13$

In one gram of sample containing 9.76% toluene and 91.24% bitumen there are $0.0976 \div 92.13 = 0.001059$ moles of toluene and $0.9124 \div 574 = 0.0015896$ moles of bitumen. The total number of moles of material in one gram = 0.0026486 and the theoretical number-average molecular weight is 380.

On the other hand, the vapor pressure of some of the lighter components of bitumens and heavy oils may be sufficiently high to cause erroneously high results from VPO measurements. For example, the determination of the average molecular weight of bitumen-toluene mixtures by VPO at 60°C illustrated that light components can be lost during the analysis.[12] Experimental and theoretical number-average molecular weights for a series of bitumen-toluene mixtures are compared in Table 7.3. The bitumen used in this work was a coker feed bitumen from Syncrude Canada Ltd. with an initial boiling point of 230°C.

Although Table 7.3 is an extreme case of the effect of light ends, it illustrates both the theoretical sensitivity of number-average molecular weight to the smaller molecules in a material, and also that these materials may cause reduced condensation on the sample thermistor leading to erroneously high results.

Volatilization of the light components of a fraction causes high results for two reasons. First, it will cause a measurable reduction in the weight concentration, (C) of the sample in solution. Referring then to the equation,

$$M_n = \frac{K}{[V/C]} \tag{4}$$

where K is the instrument constant, V is the voltage drop across the thermistors which is proportional to ΔT and C, the molar concentration, one can imagine two cases. In the first

$$M_n = \frac{K}{[V/C_W]} \tag{5}$$

and is based upon the weighed concentration of the sample. In the second,

$$M_n = \frac{K}{[V/C_A]} \tag{6}$$

and is based upon the actual concentration at the time of measurement. For a measured value of V, because $C_A < C_w$, calculations based upon C_w will give an erroneously high estimate of M_n.

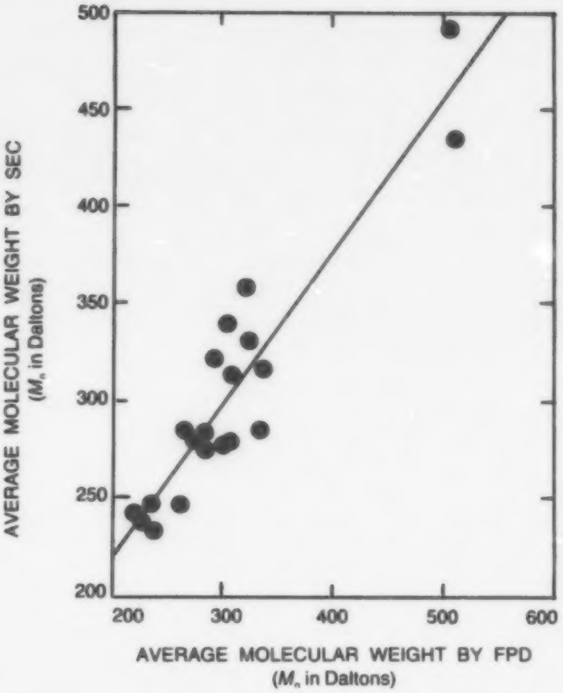

Figure 7.2: **Comparison of Average Molecular Weight (M_n) Measurements on Residues Using SEC and FPD Data from Reference 10** The best fitting straight line is $y = 0.79x + 64.0$. The standard deviations of the slope and intercept are 0.07 and 22.0 respectively.

In the case of bitumens and heavy oils, the weight loss of the sample (C_w-C_A) may be small compared to the decrease in V brought about the selective volatilization of low molecular weight compounds. In either case, a high estimate for M_n will result.

The presence of low boiling point components is indicated by drifting of the osmometer readings over extended periods. If a reading is not taken until after the drifting stops, high molecular weight values result. Given that the initial boiling point of all of the heavy oils and most of the bitumens in Alberta lie below 200°C, it is probable that most VPO measurements of these materials provide biased estimates of their number-average molecular weight.

Comparison of FPD and SEC Number-Average Molecular Weights

The comparability of data obtained by SEC and a colligative property depends upon the exact methods used. Guieze and Williams' SEC method for determining the number-average molecular weight of residues gave data equivalent to values obtained by cryoscopy.[10] A comparison of results for twenty residues from their work is provided in Figure 7.2. The value of this particular SEC method lies not only in its speed and simplicity, but in the fact that the developers of the method provided correlations between it and an established method. The method, however, relies on an initial calibration using FPD determinations of the fractions from "typical" test samples. Elution time depends on the structure of the compound as well as its molecular weight.[11]

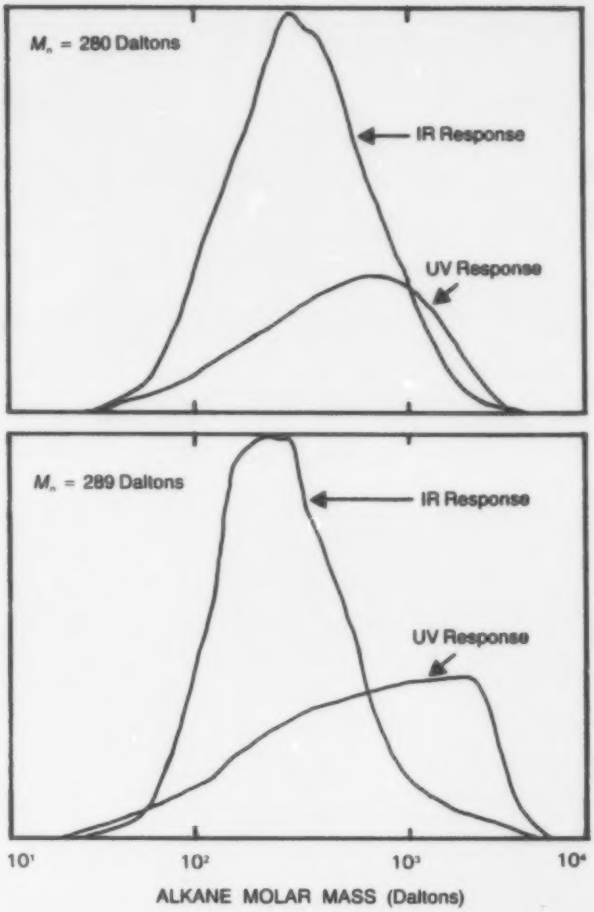

Figure 7.3: **Example of Differences in Distribution for Two Residues with the Same Average Molecular Weight (M_n)** (Reprinted with permission from J. Chrom. 1984, 312, 261-271.)

Size exclusion chromatography provides an analyst with the ability to distinguish between two or more materials whose number-average molecular weights are similar. Guieze and Williams provided chromatograms, reproduced in Figure 7.3, from their UV-IR detectors to illustrate this point. Given this figure and the sensitivity of number-average molecular weight to small molecules (provided they do not volatilize during analysis), size exclusion chromatography provides much more valuable information than either of the other methods described.

Other Factors in VPO Measurements

Numerous factors not described previously can contribute to inaccuracy and imprecision in the determination of average molecular weights by VPO for samples with an IBP above 200°C. These factors are briefly described below.

- The measuring chamber of the osmometer must be clean. Contamination, particularly with volatiles, causes slow response and poor repeatability. The thermistors must be cleaned regularly to prevent the buildup of insoluble material.
- The instrument should be in a temperature-controlled, draft-free environment.
- The bridge current must be maintained at the same value for a given solvent so that the calibration factor does not change.
- Temperature matching should be carried out each time the temperature is changed, or if the baseline of the blank begins to drift.
- Both syringes should be filled with fresh solvent before starting a blank run.
- Air bubbles must be removed from the syringe to prevent spikes in the baseline.
- The temperature setting for each solvent should be adjusted so the vapor pressure of the pure solvent is between 50 and 200 mm Hg.
- Standard benzil solutions are unstable and should be prepared daily. Sucrose octaacetate may be a more suitable standard for bitumen due to its higher molecular weight, but it tends to form very fine precipitates which are difficult to see.[14] As a result major errors in calibration can occur.
- The presence of insoluble matter in a test sample also results in high average molecular weights. The magnitude of this effect can be calculated in a similar manner to that shown in Table 2 for residual toluene. A bitumen whose true average molecular weight is 500 but which contains $x\%$ solids will yield an experimental value which is $x\%$ high.

SUMMARY

UOP 676 and ASTM D2503 are not appropriate for the determination of average molecular weights of petroleum samples with initial boiling points below 200°C. As most bitumens and heavy oils have lower initial boiling points, data obtained by these methods are probably biased toward higher values. The differences between FPD and VPO results for bitumens may be explained by the loss of light ends during VPO measurements and condensation problems during FPD measurements.

Reported molecular weights are a function of the conditions of the test. If a sample is analyzed by VPO, data should be accompanied by details of the method, solvent, sample concentrations used, and the temperature at which the measurements were taken. Until it is proven unnecessary, extrapolation to zero concentration should be used to estimate molecular weight, rather than replicate measurements at one concentration.

Size exclusion chromatography is a more versatile and useful tool for measuring molecular weight properties than either FPO or VPO. Good correlation between one SEC method and cryoscopy has been reported.

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Chapter 8: TOTAL ACID NUMBER

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TOTAL ACID NUMBER

DEFINITION

Total acid number is the quantity of base, expressed in milligrams of potassium hydroxide, required to neutralize the acidic constituents in one gram of bitumen under the conditions of the test.

SIGNIFICANCE

Correlations have been established between the acid number of heavy oils produced in a fireflood and the location of the firefront. An increase in the acid number of an oil can lead to increasing emulsion stability and therefore emulsion-treating difficulties.[3]

Severely weathered bitumen such as that found in outcrops is more acidic than unoxidized bitumen from deeper within the deposit.

Acidity generally increases with viscosity for heavy oils and bitumens but no reason for this correlation has been established.

METHODS

1. IP 213: Acidity of Bitumen: Neutralization Value

1.1 Application

This standard describes the determination of the neutralization value of asphalt (bitumen).

1.2 Summary of the Method

A potassium hydroxide solution (0.1N in distilled water), standardized by potentiometric titration with potassium hydrogen phthalate, is used to titrate bitumen dissolved in a toluene-ethanol-water solution. Excess base is added and the mixture is back-titrated with 0.1N standardized hydrochloric acid to an alkali blue endpoint.

The color change, which is clearer when back-titrating than in direct titration, can be observed in the titration beaker even though the bitumen solution is quite dark. Alternatively, it can be viewed by drawing small portions into the capillary tube of a Pasteur pipet after addition of each drop of acid.

1.3 Precision

	Repeatability[4] (mg KOH/g bitumen)
Athabasca Bitumen	
TAN ~ 2.5	0.5

2. ASTM D664: Neutralization Number by Potentiometric Titration

2.1 Application

This method covers procedures for determining acidic or basic constituents in petroleum products and lubricants.

2.2 Summary of the Method

A sample of bitumen dissolved in a toluene/water/isopropanol (50.0:0.5:49.5) solution is titrated potentiometrically with 0.1N alcoholic KOH using a glass indicating electrode and a calomel reference electrode. The endpoint is determined either graphically, or if no inflections in the curve are apparent, by titration to a meter reading for a standard buffer solution.

2.3 Precision

Graphical Determination of Endpoint

	Repeatability (% Relative)		Reproducibility (% Relative)	
Titration Mode	Manual	Automatic	Manual	Automatic
Percent	7	6	20	28

Buffer Endpoint

	Repeatability (% Relative)		Reproducibility (% Relative)	
Titration Mode	Manual	Automatic	Manual	Automatic
Percent	5	12	39	44

In the Phillips cooperative study, five laboratories determined the acid numbers of a California heavy oil blend (TAN ~ 0.25) and a Maya crude (TAN ~ 0.15) by ASTM D664. One lab reported values four times as high as the others.[4] Excluding outlying data from one laboratory, repeatability and reproducibility values of 0.07 and 0.13 mg. KOH/g of bitumen were obtained. These correspond to approximately 35 and 65% of the mean.

3. Modified IP 213 - ASTM D6641

3.1 Application

This method covers the determination of the acid number of bitumen and heavy oils.

3.2 Summary of the Method

This method, developed at the Alberta Research Council, uses the solvent systems and reagents specified in IP 213 but with a direct potentiometric titration employing 0.1N aqueous KOH. A Metrohm 636 titroprocessor in combination with a LiCl combination electrode (Metrohm 6.0276.000) gives the sensitivity required to identify the endpoint by inflection.

3.3 Precision

Repeatability
5% relative

DISCUSSION

Factors Affecting Results from IP 213

Wallace and Henry conducted a full-factorial experiment to determine the effect on the acid number of varying the amount of water in the indicator (the standard specifies a water content of ~15%), the length of time to conduct the titration and sample size.[6] The factor levels and results are summarized in Table 8.1. As the length of time taken to complete the titration and the sample size increased, the measured acid number decreased. This was attributed to precipitation of some of the acidic components with increasing time and concentration.

Therefore, while IP 213 specifies a fixed test sample size of 5 g, the strategy described in ASTM D664 of decreasing test sample size with increasing acid number is more appropriate. Bitumen usually presents a severe precipitation problem, so consideration should be given to reducing test portion sizes below those given in ASTM D664. The use of other solvent systems which may keep more of the bitumen in solution and of more concentrated KOH to reduce titration time should also be considered.

In any colorimetric titration, reproducibility can be affected by analysts' perceptions of the endpoint. Before IP 213 was converted to a potentiometric titration, analysts at the Alberta Research Council determined the end point spectrophotometrically.[6] The solution being titrated was pumped by a peristaltic pump through a continuous flow cell in a spectrophotometer with a photodiode array detector. The endpoint, defined as the point at which absorbances at 496 nm and 598 nm are equal, fell in the range identified visually by several analysts. This method did have a serious problem because precipitation of some fractions of the bitumen decreased the transmittance of light through the cell.

ASTM D974 and ASTM D3339 are also colorimetric titrations used to determine the acid number of petroleum products and lubricants by titration with 0.1N KOH in a toluene-isopropyl alcohol mixture to a p-Naptholbenzein indicator endpoint. Their application for titration of heavy oils and bitumens has not been reported due to the difficulty in detecting the color change from orange to green-brown.

Factors Affecting Potentiometric Titrations

Precipitation of asphaltenes on the electrodes during a potentiometric titration can delay the response of the electrode. When the precipitation problem is severe, inflections in the titration curve cannot be identified and titration to a buffer endpoint becomes slow and imprecise. Parker and Chung replaced the titration solvent system specified in ASTM D664 with a mixture of toluene/water/isopropanol/tetrahydrofuran (50.0:0.5:24.5:25.0) to eliminate precipitation.[3]

Parker and Chung also estimated the effects of water and accompanying suspended solids on the acid number determined by ASTM D664. For a Battrum heavy oil (TAN = 0.3) each gram of suspended solids per 100 mL of oil caused an increase of 0.1 in the acid number. Reported acid numbers decreased for samples from which solids were removed by centrifugation. This trend probably would be apparent regardless of the analytical method used.

The selection of the titration solvent and electrodes described in ASTM D664 was based on an exhaustive study conducted by Lykken and co-workers at the Shell Development Company in the 1940s.[2] They described the suitability of 41 combinations of solvent and electrode systems in terms of solvent strength, electrode equilibration rate, electrical conductivity, acidity and reactivity of the solvent and clarity of the inflection point. Their work indicates that while chloroform may increase the solvating power of the titration solvent, it is slightly reactive in combination with certain other solvents, leading to high acid numbers.

Lykken also documented the deterioration in performance of glass electrodes which are used extensively or immersed in nonaqueous solvents for long periods. Even if the electrode is immersed in water prior to every titration, continued use causes it to fail to measure hydrogen-ion activity accurately. Electrodes used in acid number determinations should be cleaned thoroughly after each titration and standardized frequently. ASTM D664 describes a test for assessing the condition of the electrode system.

Comparison of Methods

Data collected at the Alberta Research Council (Table 8.2) indicate that good agreement can be expected between the IP colorimetric procedure and the modified potentiometric titration.[3] The "accuracy" of the data was supported by a thermometric (calorimetric) titration in which the heat of neutralization was measured. The latter method was not discussed there because it is impractical for routine analyses.

SUMMARY

Determination of the acid number of bitumen and heavy oils is subject to large uncertainties due to the problem of precipitation of components during titration. Reduction of test sample size, use of alternate solvent systems and minimizing titration time, possibly by using a more concentrated titrant, may improve precision. These factors should be examined to establish a method suitable for analysis of bitumen and heavy oil.

Table 8.1: Determination of Significant Factors when IP 213 is Applied to Athabasca Bitumen.[6] The absolute value of the effect for each column is compared to $[MIN]_{95}$ to determine if the effect is significant at the 95% level of confidence.

Trial	Mean	X_1	X_2	X_1X_2	X_3	X_1X_3	X_2X_3	$X_1X_2X_3$	TAN 1	TAN 2	TAN $\bar{x}$
1	+	−	−	+	−	+	+	−	2.97	3.66	3.315
2	+	+	−	−	−	−	+	+	3.03	3.31	3.170
3	+	−	+	−	−	+	−	+	2.50	2.62	2.560
4	+	+	+	+	−	−	−	−	2.67	2.95	2.810
5	+	−	−	+	+	−	−	+	2.39	2.42	2.405
6	+	+	−	−	+	+	−	−	2.40	2.36	2.380
7	+	−	+	−	+	−	+	−	2.46	2.57	2.515
8	+	+	+	+	+	+	+	+	2.41	2.25	2.330
Mean +		2.673	2.554	2.715	2.408	2.646	2.833	2.616	Midpoint Values		
Mean −		2.699	2.819	2.656	2.964	2.725	2.539	2.755	2.52	2.49	
Effect		−0.026	−0.265	0.059	−0.556	−0.079	0.294	−0.139	2.68	2.35	2.510

$$[min]_{95} = t_{95}\, s_{pooled} \sqrt{2/mk}$$
$$= 2.20 \times 0.19 \times 0.5 = 0.21$$

where m = number of trials ÷ 2 = 4, k = number of replicates per trial = 2, and t_{95} = Student's t value at the 95% level of confidence.

X_1: Percent water in indicator
+ = 30%
− = 0%

X_2: Time delay between initial titration and back titration
+ = 10 min.
− = 0 min.

X_3: Sample size
+ = 9 grams
− = 1 gram

Table 8.2: Comparison of Various Methods for Determining Acid Number[5]

	Acid Number (mg KOH/g sample)		
	IP 213	ARC potentiometric method	Thermometric titration
Athabasca bitumen	2.31	2.35	2.45
Lloydminster heavy oil	0.68	0.76	0.84
Peace River bitumen	3.58	3.39	3.60

Acid number values determined by titration to a buffer endpoint are imprecise. If inflections in the titration curve cannot be found, data should not be reported.

The solvent system and sample concentrations used in the analysis should accompany the acid number value.

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Chapter 9: DENSITY, RELATIVE DENSITY AND API GRAVITY

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DENSITY, RELATIVE DENSITY, AND API GRAVITY

DEFINITIONS

Density is the weight in vacuo (the mass) of a unit volume of the test material at any given temperature. The SI unit of density is kg/m^3 at a specified temperature, usually 15°C. Density frequently is expressed as g/cm^3

Relative density (specific gravity) is the ratio of the weight in vacuo (the mass) of a given volume of material at a temperature, t_1, to the mass of an equal volume of water at a reference temperature, t_2. This is the same as the ratio of the density of the material at t_1 to the density of water at t_2. No units are associated with relative density but the temperatures t_1 and t_2 must be specified.

API gravity is defined as

$$°\text{API} = \frac{141.5}{\text{Relative Density } (15°\text{C}/15°\text{C})} - 131.5 \quad (1)$$

SIGNIFICANCE

API gravity is one criterion used in setting prices for crude oils. In the United States, the classification of a reservoir and the accompanying tax and royalty concessions depend in part on the API gravity of the crude.

Relative density is used in the calculation of the specific heat of petroleum. Density is used in the conversion between absolute and kinematic viscosities.

METHODS

1. ASTM D70: Specific Gravity and Density of Semi-Solid Bituminous Materials

1.1 Application

This method covers the determination of the density at 15°C or 25°C and of the relative density at 15°C/15°C or 25°C/25°C of semisolid bituminous materials.

The volume of a wide-mouthed pycnometer is determined from the difference in weights of the pycnometer when empty (A) and when filled with distilled water (B). The pycnometer is dried and reweighed with a test portion of bitumen in it (C). It is then refilled with water and weighed (D). The relative density is

$$\frac{C-A}{(B-A)-(D-C)} \qquad (2)$$

This method cannot be used for materials with a relative density less than one. For such samples, a Bingham pycnometer as described in ASTM D1217 may be more appropriate.

1.3 Precision (Relative Density)

	Repeatability	Reproducibility
ASTM	0.0035	0.0067
ACOSA		
Athabasca[a,c]	0.0079	0.0149
Lloydminster[b,c]	0.0037	0.0045
Wallace[d]	0.0026	–

[a] From triplicate analyses by nine laboratories of an Athabasca bitumen with a relative density (15°C/15°C) of 1.004.

[b] From triplicate analyses by ten laboratories of a Lloydminster heavy oil with a relative density (15°C/15°C) of 0.971.

[c] Participants in this study stated that they used a pycnometer but did not specify ASTM D70. It is unlikely that any other method could have been followed given the nature of the samples.

[d] Repeatability was estimated from the pooled standard deviation of the ASTM D70 data in Table 9.1.

2. ASTM D4052: Density and Relative Density of Liquids by Digital Density Meter

2.1 Application

ASTM D4052 covers the determination of density of petroleum distillates and oils with viscosities below 15,000 cSt at the temperature of the test. The standard states that the method should not be applied to samples so dark in color that the absence of air bubbles in the cell cannot be established with certainty. Nevertheless, the method is being used for the analysis of bitumens and heavy oils.

2.2 Summary of the Method

A 0.7-mL sample is introduced into the oscillating tube of a density meter such as a Paar digital density meter. A change in oscillating frequency occurs as a result of the increase in mass. The frequency when the sample is in the tube is compared to that when the tube is filled with distilled water. From this ratio, the mass of the contents is determined.

Standard quartz U-tubes in a density meter are fragile and are readily broken by the pressure required to inject viscous samples. The use of stainless steel U-tubes permits injection of viscous samples and measurement of density as a function of pressure.

2.3 Precision (Relative Density)

	Repeatability	Reproducibility
ASTM[a]	0.0001	0.0005
ACOSA		
Athabasca bitumen[b]	0.0008	0.0096
Lloydminster heavy oil[b]	0.0017	0.0054
Phillips[c]	0.0020	0.0032
Wallace[d]	0.0043	–

[a] Precision statements in the standard are quoted in terms of density at 15°C: numerically, these are almost equivalent to relative density at 15°C/15°C.

[b] From triplicate analyses by five laboratories of the Athabasca bitumen and Lloydminster heavy oil samples described in section 1.3.

[c] From duplicate analyses by five laboratories of a California blend with a relative density (15°C/15°C) of 0.945 and a Maya crude with a relative density (15°C/15°C) of 0.942.

[d] Repeatability was estimated from the pooled standard deviation of the ASTM D4052 data in Table 9.1.

3. ASTM D71: Density of Solid Pitch and Asphalt (Displacement Method) and Alberta Research Council (ARC) Modification

3.1 Application

ASTM D71 uses the principle of water displacement to determine the density of solid pitches and asphalts with softening points above 70°C. To minimize entrapment of air bubbles, the Alberta Research Council uses methanol instead of water for determining the density of bitumens and heavy oils.

3.2 Summary of the Method

ASTM D71 involves suspension of fragments of pitch or asphalt from a nichrome wire so that the weight of the test sample in air and then in water can be taken. This exact procedure cannot be used for most bitumens because they are too fluid to remain suspended on a wire.

In the ARC modified method, a small basket of platinum gauze is suspended from a thin wire and weighed, first in air and then submerged in methanol. The basket is dried and a 10-mg sample placed on it. The basket and sample are reweighed in air and methanol.

The density of the sample is calculated as follows:

$$\text{Density} = \frac{(A-B) \times \text{Density of Methanol at } t_1}{(A-B)-(C-D)} \tag{3}$$

where A = weight of the sample plus basket in air
B = weight of the basket in air
C = weight of the sample plus basket in methanol
D = weight of the basket in methanol
t_1 = temperature of the methanol

The relative density (t_1/t_2) is calculated from the ratio of the density of the sample to the density of water.

3.3 Precision (Relative Density)

	Repeatability	Reproducibility
ASTM	0.0050	0.0070
Wallace	0.0048[a]	–
	0.0064[b]	–
	0.0028[c]	–
	0.0081[d]	–

[a] Repeatability was estimated from the pooled standard deviation of the modified ASTM D71 data in Table 9.1.

[b] From duplicate analyses of 48 samples of Athabasca bitumen.[9]

[c] Two test samples of Athabasca bitumen (relative density at 15°C/15°C of 1.003) were prepared using eight different extraction conditions and analyzed. Repeatability includes the random error due to sample preparation under each set of conditions.[10]

[d] As in c but for Asphalt Ridge bitumen (relative density at 15°C/15°C of 0.989). The larger repeatability value was attributed to a larger variation in solids in the test samples of bitumen and an inability to make accurate corrections for those solids.[10]

4. ASTM D1298: Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

4.1 Application

This method can be used to determine the density, relative density or API gravity of bitumens and heavy oils using glass hydrometers with appropriate scales. ASTM D1250 provides conversions among the units.

4.2 Summary of the Method

A sample is brought to the prescribed temperature and transferred to a cylinder at the same temperature. The hydrometer is lowered into the sample and allowed to settle until temperature equilibrium has been reached. The hydrometer scale is read and the temperature of the sample recorded. The standard provides detailed instructions on reading the hydrometer scale and applying a meniscus correction.

4.3 Precision (Relative Density)

	Repeatability	Reproducibility
ASTM[a]	0.0006	0.0015
Phillips[b]	0.0009	0.0061

[a] For opaque samples.

[b] From duplicate analyses by five laboratories of a California heavy oil blend (relative density at 15°C/15°C of 0.944) and a Maya crude (relative density at 15°C/15°C of 0.943).

DISCUSSION

The Use of ASTM D4052 for Bitumens and Heavy Oils

The precision of the density meter method for determining the density of bitumens and heavy oils tends to be poorer than for the lighter materials for which the method was designed. When analyzing heavy materials, it may be necessary to heat the test sample considerably to lower its viscosity so that it can be injected into the tube. Entrapped air bubbles are not easily seen and cause unstable readings on the meter. A steady reading implies that there are no bubbles in the tube and that the density measurement is accurate.

To circumvent these problems, some laboratories dissolve a known mass of sample in a known mass of solvent and inject the solution into the tube.[5,6] The densities of the pure solvent and the solution are used to calculate the density of the test sample. It is assumed that the volumes of the test sample and solvent are additive so that:

$$\text{Volume}_{\text{solution}} = \text{Volume}_{\text{sample}} + \text{Volume}_{\text{solvent}} \qquad (4)$$

and

$$\frac{\text{Mass}_{\text{solution}}}{\text{Density}_{\text{solution}}} = \frac{\text{Mass}_{\text{sample}}}{\text{Density}_{\text{sample}}} + \frac{\text{Mass}_{\text{solvent}}}{\text{Density}_{\text{solvent}}} \qquad (5)$$

The latter equation can be rearranged to solve for the density of the sample. Volumes of bitumen and toluene are additive between 0.0012 and 0.048 grams of bitumen per millilitre of toluene.[2]

A suitable solvent is one which completely dissolves the test sample and which differs appreciably in density from the anticipated density of the material. Xylene, toluene and 1,1,1-trichloromethane have been used as solvents in this application.[2,5,6] Precision statements have not been reported by labs using this method.

Burroughs and Goodrich described a method for determining the density of liquids by weighing the amount of sample in a calibrated microsyringe.[3] The density of diluted samples of bitumen may be used to determine the density of the original sample in the same manner as described above.

Surface Tension Effects in the Displacement and Pycnometer Methods

Even though duplicate results from the displacement method should not differ by more than 0.005, relative density determinations on the same sample may sometimes vary by 0.2 or more for no obvious reason. When precision deteriorates to this degree, one must consider the possible effects of surface tension on the accuracy of the balance readings when the basket is submerged in methanol.

Surface tension effects can be detected by constructing several sample baskets and analyzing several bitumens with each. If a basket yields a consistently lower- or higher-than-average result, a small amount of surfactant should be added to the fluid being displaced. ASTM D70 recommends the use of Alconox for water; TRS 10-80 has been added to methanol at the Alberta Research Council.

Surfactants may also reduce the adherence of air bubbles to the test sample in both the displacement and pycnometer methods. It is important that the bitumen mass does not contain cavities which can trap air as the sample is lowered into the fluid in the displacement method or as water is added to the pycnometer.

Table 9.1: Comparison of Three Methods for Determining Relative Density[8] (Each value is based on five determinations.)

	Relative density (15°C/15°C)		
	Athabasca bitumen	**Lloydminster heavy oil**	**Lloydminster heavy oil – condensate blend**
Pycnometer (ASTM D70)			
$\bar{x}$	1.0104	0.9762	0.9301[a]
s	0.0013	0.0006	0.0007
Displacement (Modified ASTM D71)			
$\bar{x}$	1.0098	0.9789	0.9484
s	0.0013	0.0018	0.0018
Density meter (ASTM D4052)			
$\bar{x}$	1.0103	0.9825	0.9320
s	0.0016	0.0020	0.0007

[a] This sample was refrigerated prior to testing. A calibrated pycnometer was then completely filled with the sample and warmed to 15°C. The excess oil was wiped from the surface of the pycnometer before final weighing.

Static electricity can also cause significant errors in the displacement method since the masses of the basket and sample are very low. If the supporting wire is attracted to the walls of the balance, the static charge can be removed by wiping the walls with a damp cloth or a dryer fabric softener prior to taking measurements.

Comparison of Methods

Wallace compared ASTM D70, ASTM D4502 and the modified ASTM D71 method for determining the densities of a bitumen, a heavy oil and a heavy oil diluted with condensate.[8] Means and standard deviations of six measurements are reported in Table 9.1. He attributed the higher results from the displacement method for the Lloydminster blend to loss of diluent.

Temperature Conversions for Density

The conversion tables in ASTM D1250 are frequently used for estimating the density of heavy crudes at one temperature when the measurement was conducted at another. These tables are based on an average expansion coefficient for a number of typical petroleum materials. Experimental data for bitumen do not always fit predictions in the tables. However, if the conversion tables are applied to bitumen densities, errors as a result of the conversion can be minimized by minimizing the difference between the actual (experimental) and desired temperatures.

Table 9.2: Comparison of Methods for Conversion of Density of a Typical Athabasca Bitumen (1000 kg/m³ at 15°C) to Density at Other Temperatures

	Predicted density (kg/m³)		
Temperature (°C)	**ASTM D1250**	**Bulkowski[1]**	**Farouq Ali[3]**
0	1010	1009	1019
25	994	994	995
50	978	978	972
75	963	963	950
100	949	947	929
125	935	932	909
150	–	916	890

In a study of Athabasca bitumen, Bulkowski and Prill determined that the formula

$$\rho_2 = \rho_1 + 0.62\ (T_1 - T_2) \qquad (6)$$

where T_2 and T_1 are given in °C, could be also used for density conversions between 0 and 150°C.[1] Farouq Ali provided another conversion:

$$\rho_t = \rho_{15C}/1 + \frac{T-20}{1047} \qquad (7)$$

In this equation ρ_{15C} is the density at 15°C and T is the temperature at which a density value ρ_t is desired.[3]

Table 9.2 compares the predicted densities at various temperatures for an Athabasca bitumen (density at 15°C = 1000 kg/m³) using the three methods of conversion.

Sampling and Sample Preparation

Often, test samples of bitumen are prepared by solvent extraction followed by rotary evaporation to remove the solvent. If extreme vacuum and temperature conditions are used, light components in the sample may also be lost and a bias will be introduced.

Centrifugation is an alternative to solvent extraction for preparing test samples of bitumen. Although this option eliminates the problems of correction for residual solvent and loss of light ends, test samples produced by this method may contain levels of water and solids that can contribute to biases in density measurements.

From theoretical considerations alone, the density of a test sample of bitumen (~ 1000 kg/m³ at 15°C) containing 0.5% solids will be in error by 3 kg/m³ if corrections are not made:

$$\frac{\text{Mass}_{\text{sample}}}{\text{Density}_{\text{sample}}} = \frac{\text{Mass}_{\text{bitumen}}}{\text{Density}_{\text{bitumen}}} + \frac{\text{Mass}_{\text{solids}}}{\text{Density}_{\text{solids}}} \qquad (8)$$

$$\frac{100}{1000} = \frac{99.5}{\text{Density}_{\text{bitumen}}} + \frac{0.5}{2600}$$

$$\text{Density}_{\text{bitumen}} = 997\ \text{kg/m}^3$$

Biases of this magnitude due to solids have been reported in two studies on preparation of test samples of bitumen.[10,11]

Wallace and co-workers estimated the relative contribution of sampling, sample preparation and measurement uncertainties when determining densities at 15°C.[9] Laboratory samples of 15 kg were collected from a multitonne bulk sample, test samples were prepared by solvent extraction, and densities were determined by displacement in methanol. Sampling, sample preparation and measurement uncertainties were estimated to be 3, 3 and 6 kg/m^3 respectively.

SUMMARY

The pycnometer method for determining density is reliable, precise and uses relatively small test samples. Because it is so time-consuming, alternatives such as the displacement, hydrometer (where there is sufficient sample), and density meter methods are used. The displacement method can be seriously affected by surface tension and static charges but can be precise and accurate if the operator is observant and skilled. The density meter provides much better precision than other methods for light oil samples but loses that advantage for heavy oils and bitumens. Measurements of diluted samples may be used to improve precision but the magnitude of the systematic errors using this approach has not yet been documented. Measurement of the density of bitumen using a density meter at an elevated temperature, and subsequent conversion to 15°C using ASTM-API petroleum density conversion tables, may cause errors due to differences in thermal properties of bitumen and standard petroleum materials.

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Chapter 10: VISCOSITY

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VISCOSITY

DEFINITION

Viscosity is the property of a substance which causes it to resist flow. Dynamic viscosity is the shear stress of the substance divided by the shear rate and is measured in centipoise (cp) or in SI units, kg/m•sec. Kinematic viscosity is a measure the resistance of a substance to gravity flow and is measured in centistokes (cst) or in SI units, m^2/sec. Kinematic viscosity multiplied by density equals dynamic viscosity. Definitions of the various terms used to describe viscosity are given in Table 10.1.

SIGNIFICANCE

The viscosity of a crude petroleum in situ must be low enough for the crude to flow under the conditions of recovery. Viscosity of bitumen and heavy oil is routinely measured during resource characterization to estimate the conditions of temperature and pressure that are required to effect flow.

Viscosity of the produced crude must also be considered when determining the proportion of crude and diluent that will permit pipeline transportation.

METHODS

1. ASTM D3205: Viscosity of Asphalt with Cone and Plate Viscometer

1.1 Application

This method can be used to determine the viscosity of an asphalt in the range of 10^3 to 10^{10} P at the temperature(s) of the test. Shear rate may vary from 10^{-3} to 10^2 sec^{-1}. For samples of low viscosity, the Brookfield cone and plate viscometer can be modified to become a spindle viscometer as described in ASTM D2983. This configuration, however, is not routinely used for bitumen or heavy oil analysis.

1.2 Summary of the Method

The sample is placed between the cone and plate assembly which is then brought to the test temperature. Weights acting through a pulley apply torque to the cone and the angular velocity of the cone is measured. Viscosity in poises and shear rate in reciprocal seconds are calculated from the angular velocity, torque, and calibration constants. Standards for calibration are available from the Cannon Instrument Company, P.O. Box 16, State College, PA. 16801.

1.3 Precision

	Approximate viscosity (cp)	Repeatability (% Relative)	Reproducibility (% Relative)
ASTM D3205	-	11	24
ACOSA[a]			
Athabasca bitumen			
25°C	35,600	7	19
60°C	1420	15	100
100°C	190	13	151
Lloydminster heavy oil			
25°C	2370	7	20
60°C	225	14	45
100°C	45	11	43
Wallace[b]			
60°C	6460	14	-

[a] From triplicate determinations by four laboratories.

[b] From analyses of two test portions from each of twenty-four laboratory samples of Athabasca bitumen.

2. IP 71/ASTM D445: Kinematic Viscosity of Transparent and Opaque Liquids and the Calculation of Dynamic Viscosity and ASTM D1270: Kinematic Viscosity of Asphalts (Bitumens) and ASTM D445/ ASTM D2170/IP 71: Kinematic Viscosity

2.1 Application

The methods cover procedures for the determination of kinematic viscosity of liquid asphalts, road oils and distillation residues of liquid asphalts, and of asphalt cements in the range of 6 to 100,000 cst at the temperature of the test.

2.2 Summary of the Method

The time is measured for a fixed volume of the liquid to flow through the capillary of a calibrated glass capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The kinematic viscosity is then calculated by multiplying the efflux time in seconds by the viscometer calibration factor. The type of viscometer used depends upon whether or not the material is opaque. Only reverse-flow viscometers are suitable for bitumen.

Table 10.1: Viscosity Terminology and Conversions

Poise — A unit of viscosity, defined as the tangential force per unit area (dynes/cm^2) required to maintain unit difference in velocity (1 cm/sec) between two parallel planes separated by 1 cm of fluid:

1 poise (P) = 1 dyne•sec/cm^2 = 1 gm/cm•sec

1 centipoise (cp) = 0.01 P = 10^{-3} Pascal•sec $(\frac{\text{kg}}{\text{m•sec}})$

Stoke (St) = Poise/Density at that temperature

1 m^2/sec = 10^4 St = 10^6 cst

	Saybolt Seconds at:				Saybolt Seconds at:		
Centistokes	**100°F**	**130°F**	**210°F**	**Centistokes**	**100°F**	**130°F**	**210°F**
2.0	32.6	32.7	32.8	28.0	132.1	132.4	133.0
3.0	36.0	36.1	36.3	30.0	140.9	141.2	141.9
4.0	39.1	39.2	39.4	32.0	149.7	150.0	150.8
5.0	42.3	42.4	42.6	34.0	158.7	159.0	159.8
6.0	45.5	45.6	45.8	36.0	167.7	168.0	168.9
7.0	48.7	48.8	49.0	38.0	176.7	177.0	177.9
8.0	52.0	52.1	52.4	40.0	185.7	186.0	187.0
9.0	55.4	55.5	55.8	42.0	194.7	195.1	196.1
10.0	58.8	58.9	59.2	44.0	203.8	204.2	205.2
11.0	62.3	62.4	62.7	46.0	213.0	213.4	214.5
12.0	65.9	66.0	66.4	48.0	222.2	222.6	223.8
14.0	73.4	73.5	73.9	50.0	231.4	231.8	233.0
16.0	81.1	81.3	81.7	60.0	277.4	277.9	279.3
18.0	89.2	89.4	89.8	70.0	323.4	324.0	325.7
20.0	97.5	97.7	98.2	80.0	369.6	370.3	372.2
22.0	106.0	106.2	106.7	90.0	415.8	416.6	418.7
24.0	114.6	114.8	115.4	100.0[a]	462.0	462.9	465.2
26.0	123.3	123.5	124.2				

[a] At higher values use the same ratio as above for 100 centistokes; e.g. 110 centistokes = 110 × 4.620 Saybolt seconds at 100°F.

To obtain the Saybolt Universal viscosity equivalent to a kinematic viscosity determined at t°F, multiply the equivalent Saybolt Universal viscosity at 100°F by 1 + (t − 100)0.000064; e.g. 10 centistokes at 210°F are equivalent to 58.8 x 1.0070, or 59.2 Saybolt Universal seconds at 210°F.

2.3 Precision

	Temperature (°C)	Viscosity (cst)	Repeatability	Reproducibility
ASTM D2170	60	<3000	1.5 cst	3.0 cst
	60	3000-6000	2.0 cst (<0.07% relative)	9.0 cst (<0.3% relative)
	60	>6000	8.9 cst (<0.15% relative)	10.0 cst (<0.17% relative)
ACOSA[a]				
Athabasca bitumen	60	1130	1.3	21.5
	100	118	3.0	9.6
Lloydminster heavy oil	60	200	3.7	18.6
	100	37	7.4	15.8
Phillips[b]				
California heavy oil	38	284	2.2	7.4
	50	140	1.3	10.5
	60	86	0.5	11.2
Maya crude	38	172	3.8	40.9
	50	91	1.8	33.9
	60	61	1.4	48.6

[a] From triplicate determinations by five laboratories.

[b] From duplicate determinations by six laboratories.[12]

3. ASTM D2171: Viscosity of Asphalts by Vacuum Capillary Viscometer

3.1 Applications

This method is used to determine the viscosity of materials in the range of 0.036 to over 200,000 poises at the temperature of the test.

3.2 Summary of the Method

The time is measured for a fixed volume of the liquid to be drawn up through a capillary tube under controlled conditions of vacuum and temperature. The viscosity in poises is calculated by multiplying the flow time in seconds by the viscometer calibration factor. Calibration standards are available from the Cannon Instrument Company (section 1.2).

3.3 Precision

	Repeatability (% Relative)	Reproducibility (% Relative)
ASTM	7	10

4. ASTM D3570: Viscosity of Bituminous Materials with a Sliding Plate Microviscometer

4.1 Application

This method describes the determination of the viscosity of bituminous materials having viscosities in the range of 10^4 to 10^9 Pa•s at the temperature(s) of the test. Shear rate may vary between 10^{-3} and 10^2 sec^{-1}.

4.2 Summary of the Method

Two variations of the method can be used to determine viscosity. In procedure A, a film of thickness 50, 100, 300, or 500 mm (depending on the viscosity of the sample and the test temperature) is placed between two matched steel plates. One of the steel plates is clamped to the viscometer frame and the other to a device for adding a load. Five different loadings are used and the displacement rate for the movable plates is recorded. Data gathered from this method permit calculation of the rate of shear, shear stress, viscosity, and shear susceptibility.

In procedure B, an asphalt film of predetermined thickness is formed between matched pairs of aluminum, steel, or glass plates. One plate is clamped in a fixed position, and the other is displaced at constant, preselected velocities. The shearing forces are measured. The rate of shear, shear stress, and viscosity are calculated from the dimensions of the specimen, displacement rate and the shearing force developed in the test. When several displacement rates are used, shear susceptibilities may also be determined for non-Newtonian materials.

4.3 Precision
Not determined.

5. ASTM D88: Saybolt Viscosity and ASTM E102: Saybolt Furol Viscosity of Bituminous Materials at High Temperatures

5.1 Application

ASTM D88 covers the empirical procedures for determining the Saybolt Universal or Saybolt Furol viscosities of petroleum products at specified temperatures between 21 and 99°C. ASTM E102 is an extension of ASTM D88; it describes the determination of Saybolt Furol viscosities of bituminous materials.

5.2 Summary of the Method

The efflux time in seconds for 60 mL of sample flowing through a calibrated orifice, is measured under carefully controlled conditions. This time is multiplied by a calibration factor and reported either in Saybolt Universal Seconds (SUS) or Saybolt Furol Seconds (SFS), depending on the viscometer used.

Viscometers with a Universal orifice are used for materials with efflux times greater than 32 seconds. A Furol orifice is used for materials with efflux times greater than 25 seconds.

5.3 Precision

	Repeatability (% Relative)	**Reproducibility (% Relative)**
ASTM	1	2

6. ASTM D1665: Engler Specific Viscosity of Tar Products and IP 212: Viscosity – Bitumen Road Emulsion

6.1 Application

This method covers the determination of the relative specific viscosities of tars and their fluid products.

6.2 Summary of the Method

The time for 200 mL of the material at 20°C to flow from the viscometer into the receiving flask is measured and divided by the time taken for 200 mL of water to flow from the instrument under similar conditions. This ratio is the viscosity in Engler degrees.

6.3 Precision

	Repeatability (% Relative)	**Reproducibility (% Relative)**
ASTM	4	6

7. IP 72: Viscosity of Cutback Bitumen and Road Oil

7.1 Application

This method determines the viscosity of cutback bitumen and road oil in arbitrary units using the Standard Tar Viscometer.

7.2 Summary of the Method

The sample is heat-treated under prescribed conditions and then brought to the test temperature in the viscometer; the time for efflux of 50 mL of the sample from the apparatus is then recorded. Two forms of the apparatus are described, differing in the size of the orifice. A 10-mm cup is used at 25°C for materials whose viscosity at that temperature and in that cup causes efflux times to exceed 15 sec, and at 40°C for materials whose viscosity at 25°C causes times to exceed 500 sec. A 4-mm cup is used at 25°C for materials whose efflux time is less than 15 sec in the 10-mm cup at 25°C.

7.3 Precision

Viscosity (Sec)	**Repeatability**	**Reproducibility**
Below 20	2 sec	2 sec
20 - 40	2 sec	10% relative
40 and Above	5% relative	10% relative

DISCUSSION

Rheological Properties of Bitumens and Heavy Oils

Dynamic viscosity, which is the ratio of shear stress to strain rate, is independent of the strain rate at which the stress is measured if the test material exhibits Newtonian behavior. If the material is pseudoplastic or thixotropic, the measured viscosity decreases with shear rate.

Dealy determined that Athabasca and Cold Lake bitumens and Lloydminster heavy oil are non-Newtonian but that they behave differently from other non-Newtonian materials such as polymer solutions and asphalts.[6] His findings, illustrated in Figure 10.1, indicate that their viscosities are constant at low shear rates but fall off rapidly at shear rates between 0.1 and 1 $\sec^{-1}$ to a second constant value. The total reduction in viscosity is about 10% of the low shear rate value. Table 10.2 describes the rheological behavior of several other samples at a variety of temperatures to support the trends in Figure 10.1.

Christensen, Lindberg and Dorrence found that the rheological model which closely resembles the non-Newtonian behavior of Asphalt Ridge bitumens is the Bingham model:[3]

$$\tau = \tau_o + \mu\epsilon \qquad (1)$$

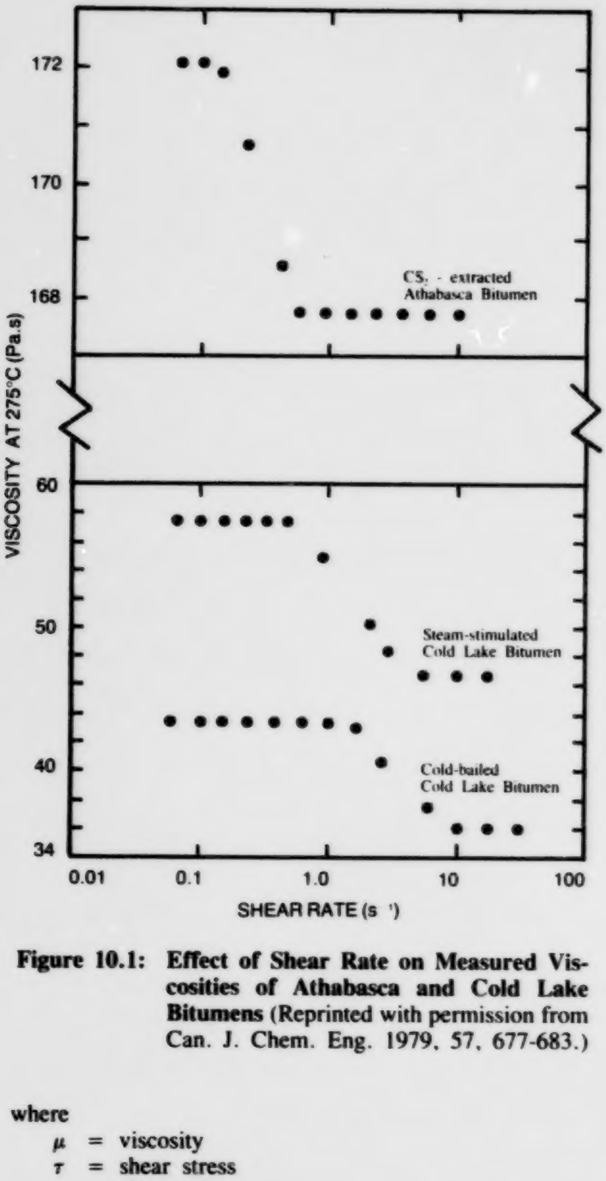

Figure 10.1: Effect of Shear Rate on Measured Viscosities of Athabasca and Cold Lake Bitumens (Reprinted with permission from Can. J. Chem. Eng. 1979, 57, 677-683.)

where

μ = viscosity
τ = shear stress
ϵ = shear rate
τ_o = shear stress required to initiate flow.

When $\tau_o = 0$, the material is Newtonian. They found that bitumen became more Newtonian with increasing temperature so that above approximately 600°C, Asphalt Ridge bitumen acts like a Newtonian liquid.

The two studies described above indicate that it is the "asphaltene" structure of bitumen which causes non-Newtonian behavior and that when this structure is broken down by heating (or by solvent addition as described by Christensen), bitumens and heavy oils act as Newtonian liquids. For analytical purposes, it is important to remember the possible non-Newtonian behavior of the sample and therefore report shear rate with the viscosity of the sample.

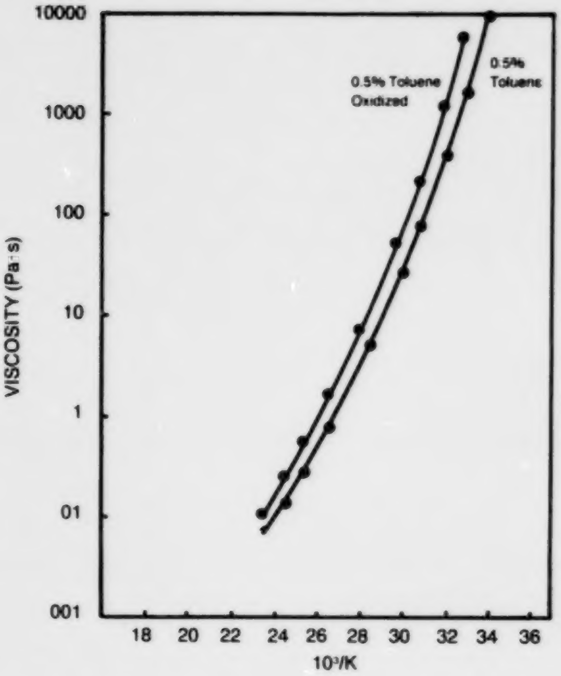

Figure 10.2: Effect of Oxidation on the Viscosity of Asphalt Ridge Bitumen (Reproduced from Fuel 1984, 63, 1313-1317, by permission of the publishers, Butterworth & Co. (Publishers Ltd.)

Errors Due to Sample Preparation

The bitumen or heavy oil in laboratory samples of emulsions and oil sand must be purified before test portions are analyzed. Solvent extraction is often used to prepare test portions, but the presence of low levels of solvent causes a large relative error in the viscosity reading. The use of more severe conditions for complete removal of the solvent causes stripping of the light components of the sample and high viscosity readings. Christensen and co-workers demonstrated that oxidation at 100°C for as little as two hours, such as might occur during reflux and extraction, can cause a significant increase in viscosity[3] (Figure 10.2).

Centrifugation has been proposed as a means of reducing the alteration of viscosity of test portions of bitumen from cores of Athabasca oil sand.[16,18] This method is limited to bitumens which flow under the extraction conditions, and often results in test portions containing approximately 0.5% solids which can damage the surfaces of a dynamic viscometer. Centrifugation can also be used for preparation of test portions from some emulsions but, again, complete removal of solids and

Table 10.2: Variation of Viscosity with Shear Rate; Essential Features of Curves (Reprinted with permission from Can. J. Chem. Eng. 1979, 57, 677-683.)

Sample	Temp. (°C)	Viscosity at infinitely low shear (Pa.s)	Viscosity at infinitely high shear (Pa.s)	Shear rate range over which η fell from η_o ($\eta\infty$, s^{-1})
1	27.5	172	168	0.15 — 0.8
	42.5	17.5	16.6	0.15 — 1.0
	72.5	3.1	2.1	0.1 — 0.5
2	27.5	170	167	0.1 — 0.4
	42.5	22.3	21.0	0.2 — 1.5
	57.5	7.3	6.65	0.1 — 0.6
	72.5	2.65	2.40	0.2 — 0.4
3	27.5	1.96	1.68	0.1 — 0.4
	42.5	0.56	0.485	0.2 — 0.4
	57.5	0.36	0.28	0.3 — 1.2
4	27.5	43.7	36.3	1 — 10
5	27.5	57.6	46.8	0.8 — 6
6	27.5	302	273	0.2 — 1.0
7	27.5	51.8	46.8	0.4 — 1.5
	40.0	12.7	12.2	0.4 — 3
	57.5	3.55	2.84	0.2 — 0.7
1[a]	27.5	286	269	0.2 — 0.6
6[b]	27.5	103	90	0.1 — 0.4
6[c]	27.5	1050	< 650	0.5 — ?

[a] Sample aged at 80°C for 48 hours.

[b] 2% toluene added.

[c] 5% asphaltenes added.

Sample Sources:
1 Athabasca CS_2-extracted bitumen
2 Cold Lake cold-bailed bitumen
3 Lloydminster primary production heavy oil
4 Cold Lake cold-bailed bitumen
5 Cold Lake steam-stimulated bitumen
6 Athabasca toluene-extracted bitumen
7 Cold Lake cold-bailed bitumen (8.4% water)

water is not guaranteed (see Chapter 16 which describes BS&W determinations).

Some laboratories extract the oil by repeated cold washings to minimize oxidation. However, the problem of completely removing the solvent without removing light components of the sample still remains. When removing solvent by rotary evaporation, some analysts attempt to trap the light ends and add them back into the sample. Any trap which will retain the light ends also retains solvent and so a clean separation of the two is difficult to attain.

Clossman and Worthman attempted to reduce the error caused by loss of light ends during solvent removal when preparing pure bitumen from field samples.[4] They first collected the light fraction by distillation and then extracted the heavy ends with solvent. After solvent removal, they blended the distillate with the heavy ends. For highly viscous materials, the conditions required to remove solvent are more severe than for fluid materials. Therefore, to remove all of the solvent from a residue, some loss of the light ends of the residue (the middle portion of the total sample) will probably occur. Errors in viscosity are probably not as great when a middle boiling point cut is lost instead of a light cut but the loss of a middle fraction may still alter the bitumen significantly for the purpose of collecting meaningful viscosity data.

A third alternative involves rotary evaporation under mild conditions to reduce the solvent level to 3 or 4% while minimizing loss of the light components, followed by mathematical correction of the viscosity for residual solvent to obtain a value for viscosity on a solvent-free basis. Of the numerous equations[1,2,5,9,10,13,14] used to predict the viscosity of mixtures from the viscosity of its pure components, and conversely, calculation of the viscosity of a component from that of a mixture and its other component, the equation of Cragoe[5] appears in principle to be the most suitable:

$$\mu_m = 5 \times 10^{-4} \exp\left[\frac{x_1}{\ln\mu_1 - \ln 5 \times 10^{-4}} + \frac{1 - x_1}{\ln\mu_2 - \ln 5 \times 10^{-4}}\right]^{-1} \quad (2)$$

where:

μ_m = viscosity of mixture (poises)
μ_1 = viscosity of bitumen (poises)
μ_2 = viscosity of solvent (poises)
x_1 = weight fraction of bitumen in the mixture.

Table 10.3: Correction of Viscosity of Athabasca Bitumen for Residual Toluene[a]

Temperature (°C)	Toluene (wt. %)		Viscosity (cp)				
				Corrected by Cragoe equation		Corrected by modified Cragoe equation	
	Before[a]	After[b]	Measured	Before[a]	After[b]	Before[a]	After[b]
25	0	0	289,800	289,800	289,800	289,800	289,800
25	0.89	0.91	187,900	399,100	406,300	306,700	310,200
25	2.57	2.55	69,720	560,400	549,800	259,600	256,600
25	4.91	4.77	22,530	1,034,700	892,400	226,300	209,000
60	0	0	4150	4150	4150	4150	4150
60	0.89	1.19	3260	5160	6080	4350	4810
60	2.57	2.26	1750	6260	5261	3820	3450
60	4.91	4.21	890	9600	6280	3610	2870
100	0	0	276	267	276	276	276
100	0.89	0.86	223	303	300	268	266
100	2.57	2.23	158	379	333	264	246
100	4.91	3.12	124	726	342	333	224

[a] Toluene was added to the bitumen, and the mixture thoroughly homogenized by spinning slowly in a round-bottomed flask. The toluene content of the mixture was measured by gas chromatography immediately before the viscosity measurements were taken.

[b] From the analysis of a test portion recovered from the viscometer immediately after viscosity measurements were taken.

[c] Toluene viscosities were assumed to be 0.005574 P at 25°C, 0.003864 P at 60°C and 0.002765 P at 100°C.

It is intuitively apparent that the effect of a given level of solvent on the viscosity of a bitumen increases with increasing viscosity of the bitumen. Cragoe's equation can be rearranged to illustrate this point.

Let $a = 5 \times 10^{-4}$ P

$$\mu_m = a \times \exp\left[\frac{x_1}{\ln\mu_1 - \ln a} + \frac{(1-x_1)}{\ln\mu_2 - \ln a}\right]^{-1}$$

The natural log of both sides of this equation yields:

$$\ln\mu_m = \ln a + \left[\frac{x_1}{\ln\mu_1 - \ln a} + \frac{(1-x_1)}{\ln\mu_2 - \ln a}\right]^{-1}$$

$$\ln\mu_m - \ln a = \left[\frac{x_1}{\ln\mu_1 - \ln a} + \frac{(1-x_1)}{\ln\mu_2 - \ln a}\right]^{-1}$$

The inverse of the equation yields:

$$\frac{1}{\ln\mu_m - \ln a} = \frac{x_1}{\ln\mu_1 - \ln a} + \frac{(1-x_1)}{\ln\mu_2 - \ln a}$$

$$= x_1 \quad \left(\frac{1}{\ln\mu_1 - \ln a} - \frac{1}{\ln\mu_2 - \ln a}\right)$$

$$+ \frac{1}{\ln\mu_2 - \ln a}$$

or

$Y = x_1D + B$ which is a straight line form.

But, D is related to B mathematically by:

$$D = \frac{1}{\ln\mu_1 - \ln a} - B \tag{3}$$

In other words, the slope of the line is dependent on the intercept. In practical terms, for a given solvent the change in viscosity with percent solvent (slope) is related to the absolute viscosity of the solvent-free bitumen (y-intercept).

As μ_2 increases, $\dfrac{1}{\ln\mu_2 - \ln a}$

decreases and therefore $\dfrac{1}{\ln\mu_1 - \ln a}$

$- \dfrac{1}{\ln\mu_2 - \ln a}$, which is the slope increases.

However, the use of the Cragoe equation to correct the viscosity of a mixture for residual solvent results in increasing over-correction with increasing solvent level. In Table 10.3, the measured viscosities of mixtures of bitumen and toluene are presented. The viscosity of the pure bitumen based on the composition and viscosity of the mixture and the viscosity of toluene is compared to the measured viscosity of the solvent-free bitumen. In columns 5 and 6, the over-correction caused by the Cragoe equation is apparent. However, if a in the Cragoe equation is set at 1×10^{-4} P the correction often falls within 15%, the repeatability of a single measurement, of the measured viscosity.

Use of the modified Cragoe equation requires an accurate estimate of the level of solvent in the mixture. At high temperatures, solvent tends to evaporate from the mixture so the amount of solvent in the test portion at the time of the measurement is not exactly known. In Table 10.3, the level of toluene in the mixture prior to and immediately following the viscosity measurement is given to illustrate the degree of toluene loss. A difference of 10% relative in the reported values for toluene is significant because it is greater than the uncertainty associated with the measurement of toluene content.

Note that for one set of measurements at 60°C, the level of toluene appeared to increase. This was attributed to toluene which remained from cleaning the viscometer after the previous run. This problem occurred more frequently in subsequent runs at 15°C.

Errors Due to Sampling in the Determination of Viscosity

The viscosity of a test sample of bitumen or heavy oil can be affected by the methods used to collect the laboratory sample as well as treatment of the laboratory sample to produce the test sample. Gibson stated that invasion of drilling and treatment fluids during coring, and expansion of the formation gases and liquids when bringing cores to the surface are inevitable.[7] When collecting cores for subsequent measurements of bitumen viscosity he recommended that water-based mud systems with cation concentrations approximating those of the formation fluids be used, surfactants and other treatment chemicals should not be used without an understanding of their impact on the properties of the oil, and high-pH muds and pump pressures should not be used as they may flush some of the oil from the core.

After the core is retrieved, it should be stored in a manner that will minimize oxidation and loss of the light ends. Cores are usually encased and sealed in plastic sleeves in the core barrels, and then frozen. In special circumstances, cores are collected in pressurized steel barrels to prevent loss of light ends. Recovery of the core from the barrel involves cutting open the barrel at liquid-nitrogen temperature.

When samples are obtained by cold-bailing, precautions should be taken to ensure that they have not been contaminated with diluents or chemical additives downhole. Chemical pumps should be turned off and lines flushed prior to sampling.

The contribution of systematic errors or biases due to the presence of residual solvent and the loss of light ends from a test sample has been discussed in the preceding section. Wallace and co-workers estimated the relative repeatability for viscosity measurement at 60°C (ASTM D3205) and for preparing a test sample of bitumen from a homogenized sample of oil sand to be approximately 13.5%.[15] The random error due to sample preparation is not considered in the ASTM standards which estimate measurement error alone. Within a 50-tonne lot of oil sand, the variability in the viscosity at 60°C was found to be four times as large as the uncertainty in the measurement when 15-kg samples of oil sand were taken. Therefore, approximately 40 such samples would need to be collected, extracted and analyzed to ensure that mean viscosity would be within 10% of the average viscosity of the bitumen, at the 95% level of confidence. The variability for smaller laboratory samples was not identified.

Table 10.4: Correction of Viscosity of Athabasca Bitumen for Naphtha Content[17]

	Viscosity (cp)		
	Measured	Corrected	
Naphtha (wt. %)		Cragoe	Modified Cragoe
0.0	251,000	251,000	251,000
1.66	106,000	379,000	245,000
3.40	49,500	651,000	255,000
4.85	25,700	933,000	238,000
8.20	5,650	1.4×10^6	145,000
100	0.624	—	—

Comparison of Viscometers

Of the seven methods for determining viscosity described in this chapter, only two, ASTM D445 and ASTM D3205, were used widely enough in the ACOSA and Phillips cooperative studies to generate estimates of precision. Both studies confirmed the ASTM findings that the former method is more repeatable. Reproducibility in the ACOSA and Phillips studies was poor compared to the ASTM statements. Errors in calibration frequently cause poor reproducibility. A National Bureau of Standards Monograph[11] describes calibration of viscometers using liquids of known viscosity and reference viscometers. The monograph is too extensive to paraphrase here but it should be read by anyone carrying out kinematic viscosity measurements.

The vacuum capillary viscometer can be imprecise because of difficulties in maintaining a constant vacuum and obtaining a reliable measurement of the vacuum. The Saybolt viscometers, Engler specific viscometer, and the Standard tar viscometer are not practical for universal use because results in centipoise or centistokes are required in most calculations. The International Standards Organization has requested that viscosity measurements should be metricated during the next few years. When this occurs methods such as ASTM D88, ASTM D1665, ASTM E102, IP212 and IP72 may no longer be accepted as standard methods.

When converting between kinematic and dynamic viscosities, the precision of the density term used in the conversion (Table 10.1) must be considered as part of the precision of the viscosity value. Both kinematic and dynamic viscosities are required by data users and one would expect that a viscometer giving a reading in the required units should be the method of choice. However, the relative repeatability of a density measurement is so small compared to the difference in repeatabilities between ASTM D445 and ASTM D3205 that, on the basis of precision considerations alone, the former should be used for both kinematic and dynamic viscosity measurements. Cone-and-plate viscometers as in ASTM D3205 also require more extensive maintenance programs and are more easily damaged by samples containing solids.

SUMMARY

Of the seven methods for measuring viscosity described in this chapter, ASTM D3205 (a dynamic viscosity method) and ASTM D445 (a kinematic viscosity method) are the most frequently used because they provide data in units which are directly applicable in engineering calculations. From the consideration of precision alone, both dynamic and kinematic viscosities should be determined on the basis of ASTM D445 measurements because that method is more precise than ASTM D3205. The ACOSA and Phillips cooperative studies indicated that depending upon the sample and temperature of the test, the reproducibility of ASTM D445 ranged from approximately 10 to 50%. These data were obtained using homogenized samples of bitumen.

The viscosity of a crude as it exists in the original oil sand is often needed so a test sample must be prepared before taking analytical measurements. Even in small (50- to 100-tonne) lots of oil sand, the contribution of sample variability is severe so that many (perhaps up to 40) increments must be collected and analyzed to hold the uncertainty of the mean to 10% relative at the 95% level of confidence. Systematic errors due to the presence of residual solvent in the sample, and stripping of the light components from the sample can also be large. Further work to develop a formula that will mathematically correct viscosity for residual solvent content is required.

Several laboratories are developing ultracentrifugation methods to prepare test samples of bitumen from oil sand. Because the bitumen is not exposed to heat or solvent, the method should provide an unaltered test sample. No papers describing ultracentrifugation in this context have been published.

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Chapter 11: ASPHALTENES

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ASPHALTENES

DEFINITION

Asphaltenes are the components of bitumen which are soluble in toluene and which precipitate from solutions of normal paraffins under specified test conditions. Thus, asphaltenes are based upon solubility parameters and are not specific chemical components.

SIGNIFICANCE

Asphaltenes are probably the most thoroughly researched yet least understood components of crude oils. The level of asphaltenes or heavy components in a crude is the major factor distinguishing heavy oils and bitumens from conventional crudes. Yen stated that "the amount of heavy fractions in a given crude or bitumen is responsible for the extent that the viscosity and density (specific gravity) increase or decrease. Removal or reduction of asphaltene or preasphaltene will drastically alter the association behavior and thus affect the rheological properties of a given oil."[25] The presence or absence of asphaltenes is the basis for some bitumen classification schemes.[25]

However, the chemical composition of asphaltenes from different deposits has been shown to vary widely, bringing into question the validity of these schemes.[22] One researcher also concluded that asphaltenes (of a bitumen from Utah) are "chemically nondefinitive in terms of compound types, functionality, or other structural features."[3] This review will not attempt to determine which opinion is more correct. Rather, the arguments should stimulate data users to ask whether or not an asphaltene measurement is the most appropriate one for resolving their problem.

Asphaltene measurements are used in the preliminary assessment of a petroleum resource. The asphaltene fraction is significant as it is a major precursor of coke.[21] Asphaltene in conjunction with carbon residue tests are therefore a measure of relative feedstock quality for upgraders. Relationships between asphaltene and carbon residue values are illustrated in Figures 11.1 and 11.2. Asphaltene measurements can also be used in support of, but not as a replacement for, tests which more directly address physical properties such as viscosity and density of a crude. Asphaltene measurements are most appropriate when assessing feedstock for solvent deasphalting processes. The analytical method of choice will then be one which approximates the commercial process.

The conditions under which asphaltene precipitation begins, has been used to determine the most appropriate diluent for a given crude for emulsion dehydration and to produce a blend suitable for pipelining.[1,19] Numerous references describe the determination of asphaltenes by gel permeation and thin layer chromatography.[2,8,16,18] Neither subject will be discussed in detail here.

METHODS

1. **Syncrude Analytical Method 5.1: Analysis for Saturates, Aromatics, Resins and Asphaltenes in Bitumen by Liquid-Solid Chromatography.**

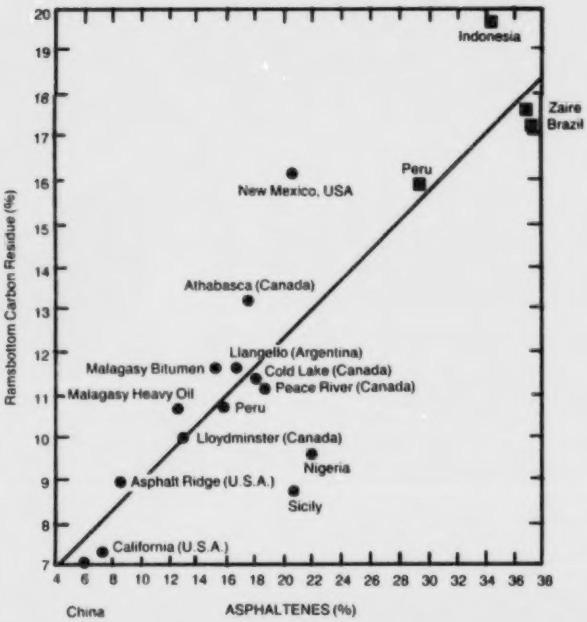

Figure 11.1: **Relationship Between Asphaltene Content (Syncrude Analytical Method 5.1) and Ramsbottom Carbon Residue for Bitumen Samples from Around the World**[22] The best-fitting straight line is $y = 0.35x + 5.45$. The standard deviations of the slope and intercept are 0.05 and 1.0 respectively. Squares denote samples which were severely weathered before sampling.

1.1 Application

This method describes the precipitation of asphaltenes from bitumen and subsequent separation of the maltenes.

1.2 Summary of the Method

A 2- to 3-g sample of bitumen is dissolved in a volume of benzene numerically equal in millilitres to the weight of the sample in grams. A volume of pentane equal to forty times the volume of the benzene is added. The mixture is shaken initially for 5 minutes, and then briefly shaken at 30-minute intervals over an elapsed time of 2 hours. The mixture is kept in the dark during precipitation. The asphaltenes are collected on a medium-pore fritted glass filter, washed with pentane, dried and weighed. The maltene fractions are then separated on clay and silica columns. Since publication of the method, Syncrude has substituted toluene for benzene for dissolving the original sample.

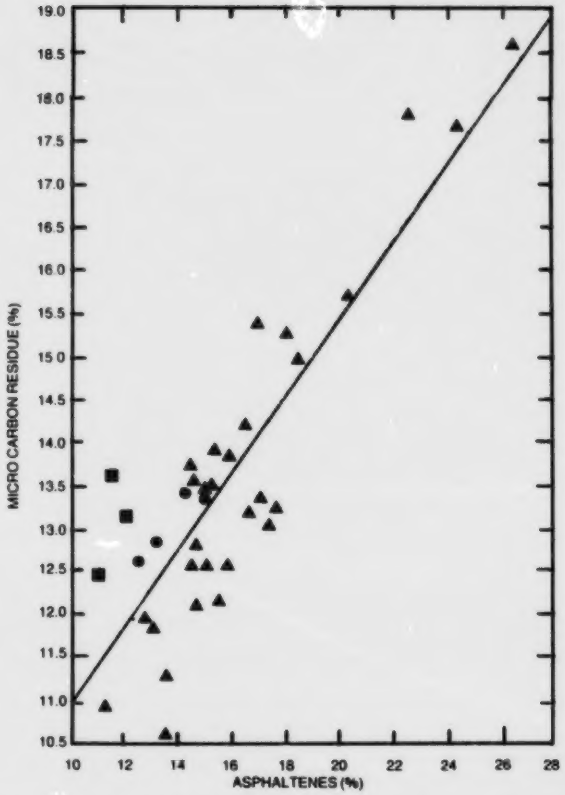

Figure 11.2: **Relationship Between Asphaltene Content and Micro Carbon Residue for Bitumen Samples from Alberta**[6] The best-fitting straight line is $y = 0.44x + 6.59$. The standard deviations of the slope and intercept are 0.04 and 0.63 respectively. Asphaltenes were precipitated from a 60:1:1 mixture of n-hexane:bitumen methylene chloride by shaking for sixteen hours. The precipitate was collected on a Whatman No. 5 filter paper. Samples from the Cold Lake (■), Athabasca (•) and Peace River deposits (▲) were analyzed.

1.3 Precision

	Repeatability (% Relative)	Reproducibility (% Relative)
Syncrude Method 5.1	3.1	-
ACOSA[a]	14.2(5.9)	18.3
Phillips[b]	7.4	45.2
Alberta Research Council	4.5[c]	-
	5.3[d]	-
	11.6[e]	-
	5.5[f]	-

[a] From triplicate analyses by five laboratories of an Athabasca bitumen containing 15% asphaltenes and a Lloydminster heavy oil containing 13% asphaltenes. In the cooperative study, one laboratory's repeatability was double that of any others. The overall repeatability calculated without that data is given in brackets.

[b] From duplicate analyses by three laboratories of a California blend and a Maya crude each containing approximately 14% asphaltenes. One laboratory reported values approximately 5% absolute higher than the other two.[13]

[c] From triplicate analyses of an Athabasca, a Cold Lake and a Peace River bitumen. These samples contained 15, 17 and 17% asphaltenes as defined by this method.[5]

[d] Two test samples of Athabasca bitumen (17% asphaltenes) were prepared using eight different extraction conditions and analyzed. Repeatability includes the random error due to sample preparation under each set of conditions.[21]

[e] As in d but for Asphalt Ridge bitumen (8% asphaltenes). The larger repeatability value was attributed to a larger variation in solids in the test samples of bitumen and an inability to make accurate corrections for those solids.[23]

[f] This estimate of repeatability includes random error from the Soxhlet extraction, solvent-removal and measurement steps of the analysis of an Athabasca bitumen containing 18% asphaltenes. Forty-eight samples were extracted and analyzed in this study.[24]

2. UOP 99-82: Pentane-Insoluble Matter in Petroleum Oils Using a Membrane Filter

2.1 Application

This method is used to measure the amount of pentane-insoluble matter in petroleum oils that are reasonably fluid at 37°C or lower temperatures, or which are hard at dry-ice temperature. Samples that cannot be completely dispersed in n-pentane by digestion at 37°C should not be analyzed by this method. The presence of solids invalidates the test.

2.2 Summary of the Method

A 0.5-g test sample, which contains between 5 and 20% asphaltenes, is dispersed in n-pentane by alternating digestion at 37°C with ultrasonic treatment. The mixture is shaken in a shaker water bath at 37°C for 1 hour and filtered while warm through a membrane filter with a pore size of 0.5 μm. The precipitate is washed with warm n-pentane, dried and weighed. An appendix to this method describes sampling procedures for heavy oils and asphalts.

2.3 Precision

	Repeatability (%)
2.3% pentane insolubles	0.3
22.3% pentane insolubles	3.7

3. ASTM D893: Insolubles in Used Lubricating Oils

3.1 Application

ASTM D893 was designed to determine the level of pentane and toluene insolubles in lubricating oils. The method can be used for recovering an asphaltene fraction from bitumen.

3.2 Summary of the Method

A 10-g sample is weighed and mixed with n-pentane to give a total volume of 100 mL. The mixture is centrifuged at a relative centrifugal force of 600 × to 700 × g and the oil solution decanted. The precipitate is washed twice with n-pentane, dried, and weighed.

3.3 Precision

	Repeatability (% Relative)	**Reproducibility (% Relative)**
ASTM	10	15
Alberta Research Council[a]	11.3	-

[a] From triplicate analyses of an Athabasca, a Cold Lake and a Peace River bitumen.[5] These samples contained 20, 22 and 26% asphaltenes as defined by this method.

4. ASTM D2007: Characteristic Groups in Rubber Extender and Processing Oil by the Clay Gel Adsorption Method

4.1 Application

This method is primarily intended for the separation of oil samples into polar compounds, aromatics and saturates. However, provision is made for the precipitation of n-pentane insolubles.

4.2 Summary of the Method

A 10-g sample is weighed, mixed with 100 mL of n-pentane, and the mixture is stirred while being warmed in a water bath. It is then allowed to sit at room temperature for 30 minutes. The precipitate is collected on a fine-pore fritted glass filter, washed with n-pentane, dried and weighed. The soluble fractions are subsequently separated on an attapulgus clay column.

4.3 Precision

	Repeatability (%)	**Reproducibility (%)**
ASTM[a]	<0.1	<0.1
Alberta Research Council[b]	31.4	

[a] Repeatability and reproducibility are low as materials normally analyzed by this method contain little if any asphaltenes fraction.

[b] From triplicate analyses of an Athabasca, a Cold Lake and a Peace River bitumen.[5] These samples contained 17, 21 and 26% asphaltenes respectively as defined by this method.

5. UOP 614-68: Heptane-Insoluble Matter in Petroleum Oils Using a Membrane Filter

5.1 Application

This method is used to measure heptane-insoluble materials in petroleum oils which are fluid at 80°C or below, or which are solid at dry-ice temperature. It is not appropriate for materials which cannot be completely dispersed in n-heptane.

5.2 Summary of the Method

A 0.5-g test sample, which contains between 5 and 20% heptane insolubles, is dispersed in n-heptane, digested at 80°C for 1 hour and filtered through a 0.5-μm membrane filter. The precipitate is washed with hot n-heptane and weighed. Sampling procedures for heavy oils and asphalts are described in an appendix to the method.

5.3 Precision

Not established for materials containing greater than 5% heptane-insoluble materials.

6. ASTM D4124: Separation of Asphalt into Four Fractions

6.1 Application

This method covers the separation of petroleum asphalts into n-heptane asphaltenes, saturates, naphthene aromatics, and polar aromatics.

6.2 Summary of the Method

A 12-g sample of bitumen is mixed with a volume of n-heptane equivalent in millilitres to 100 times the weight of bitumen in grams. The mixture is stirred in a stoppered flask over a steam bath at 95°C for 1 hour. The asphaltenes are allowed to settle overnight at room temperature. The mixture is then filtered through a filter paper; the filtrate is rinsed with n-heptane, dried and weighed. The standard also describes separation of the maltenes into its constituents.

6.3 Precision

Not yet determined.

7. ASTM D3279: n-Heptane Insolubles

7.1 Application

This method covers the determination of the weight percent of asphaltenes as defined by insolubility in n-heptane. It is applicable to all solid and semisolid petroleum asphalts containing little or no mineral matter, to gas oils, to heavy fuel oils, and to crude petroleum that has been topped to a cut-point of 343°C or higher.

7.2 Summary of the Method

A 1-g sample is weighed and dispersed with approximately 100 mL of n-heptane. The mixture is refluxed slowly with stirring for 15-20 minutes and cooled for 1 hour. It is then warmed slightly and filtered through a gooch crucible fitted with a glass fibre filter. The precipitate is washed with n-heptane and dried at 115°C for 15 minutes.

7.3 Precision

Repeatability (% Relative)	Reproducibility (% Relative)
1.5	2.8

8. IP 143: Asphaltenes Precipitation with n-Heptane

8.1 Application

Asphaltenes are separated from oils, bitumens, and crude petroleums which have an initial boiling point of 260°C or higher.

8.2 Summary of the Method

A sample not exceeding 10 g is dissolved in a volume of n-heptane numerically equal in millilitres to 30 times the sample weight in grams. The mixture is refluxed for an hour and allowed to sit for a further 1.5 to 2.5 hours. The insoluble material consisting of asphaltenes and waxy substances is collected by filtration through a Whatman No. 42 filter paper. Waxy constituents are extracted by hot reflux with n-heptane, and the asphaltenes are isolated by extraction with toluene or benzene.

8.3 Precision

	Repeatability (% Relative)	Reproducibility (% Relative)
ASTM	10	15
Poirier[a]	12	-

[a] From eight analyses of an Athabasca bitumen containing 12% asphaltenes and a Boscan heavy oil containing 18% asphaltenes as defined by this method.[15]

DISCUSSION

Because asphaltenes are not a distinct chemical species, attempts to define the "correct" method of determination are inappropriate. Organizations have usually developed their own data bases and correlations using specified methods, and are unlikely to change to an industry-wide standard. This discussion, therefore, centres on the effect of changing various conditions such as solvent type, solvent-bitumen ratio and precipitation time on the percentage of bitumen which precipitates. When

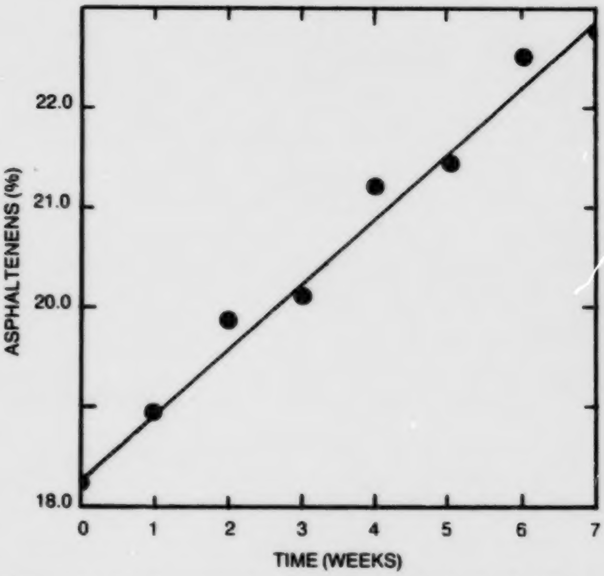

Figure 11.3: **Increase in Asphaltene Content of Athabasca Bitumen in Solution due to Photooxidation[17]**

these trends are known, those who are reviewing data obtained by a variety of methods can at least make approximate comparisons of the crudes.

The Factorial Approach to Identifying Factors Affecting Asphaltene Precipitation

Screening experiments can be used to determine the factors in an analytical method that will have the greatest impact on the result. A series of analyses are conducted in a set pattern in which each factor is assigned one of two levels. For example, in the case of asphaltenes, the effect of using a 1:25 bitumen-to-pentane ratio as compared to a 1:75 ratio can be determined. The average difference between the tests can be compared to the repeatability to determine if the difference is statistically significant.

To identify the important factors in Syncrude Analytical Method 5.1, a screening design was run at the Alberta Research Council.[5] The factors and their assigned levels are listed in Table 11.1. Factor 7, the effect of fine solids (<37-μm) in bitumen, was examined to determine if fines tend to act as nuclei for extra precipitation, or if they pass through the sintered glass frit.

The results of the experiment are given in Table 11.2. Changing the bitumen-to-pentane ratio from 1:75 to 1:25 caused a reduction in the amount of asphaltenes which was significant at the 90% level of confidence. Toluene can be substituted for benzene without changing the result of the analysis because the solvation power of these solvents as measured by the Hildebrandt solubility parameters, δ, are similar ($\delta_{benzene} = 9.2$ and $\delta_{toluene} = 8.9$).

A slight increase in asphaltene content (approximately 0.5% in magnitude) was attributed to conducting the precipitation at 25°C instead of 3°C and under lighted conditions rather than in the dark. Given the repeatability of the determination and the design of the experiment, there is a 70% chance that these increases are real and not a result of analytical uncertainty. Speight noted that a temperature increase results in better coagulation of the asphaltene particles and a reduction in the solubility of resinous material in the solvent, thereby causing increased precipitation.[20] Montgomery explained that bitumen is sensitive to photo-oxidation reactions which increase the concentration of sulfoxides; crosslinking reactions which follow tend to convert "resins" to "asphaltenes".[12] UOP 99 warns against the use of excessive digestion times when precipitating asphaltenes for the same reason.

Production of asphaltenes in solution due to photooxidation was studied over a period of seven weeks at the Alberta Research Council.[17] Approximately 50 g of Athabasca bitumen were dissolved in 2 L of toluene and allowed to sit in the sunlight in a sealed glass jar. Aliquots were taken weekly to determine the asphaltene content of the bitumen. An increase in asphaltene content was apparent as shown in Figure 11.3. While these conditions are unlikely to be duplicated in the routine operation of a lab, the results confirmed the factorial described above and also raised some questions about the reactions that occur during a Soxhlet extraction at elevated temperatures when bitumen is extracted from oil sand.

Table 11.1: **Design of Screening Experiment for Asphaltene Precipitation[5]**

Factor (X)	Upper level (+)	Lower level (−)
1. Pentane-bitumen ratio (v/v)	75:1	25:1
2. Contact time (hr)	5	0:5
3. Temperature (°C)	25	3
4. Lighting	Light	Dark
5. Pore size of filtering crucible	Fine (4-8 μm)	Medium (10-15 μm)
6. Dispersing solvent	Toluene	Benzene
7. % fines in bitumen	1% added	0% added
8. Sample weight (g)	1	3.5

Solvent Type and its Effect on Precipitation

To gain some insight into the mechanisms involved in precipitation, Mitchell and Speight precipitated "asphaltenes" from Athabasca bitumen using a variety of solvents and solvent blends.[11] The insoluble organics were separated by dissolving bitumen in an equal volume of benzene followed by dilution with 40 volumes of the specified solvent or blend. They correlated the percentage of the bitumen which precipitated to the solvent power of the precipitating solvent (Figures 11.4 and 11.5).

These experiments indicated that for Athabasca bitumen, substitution of n-heptane for n-pentane would cause a 33% relative reduction in the amount of insolubles. The average values reported in the ACOSA cooperative study for n-pentane and n-heptane insolubles in Athabasca bitumen were 15.0% and 9.8%. For Lloydminster heavy oil the corresponding values were 12.8% and 8.2%. The decrease in the percentage of precipitate as a result of using n-heptane in place of n-pentane was 35% for both materials.

Table 11.3: Precision of n-Pentane and n-Heptane Asphaltene Determinations

	Repeatability (% Relative)		Reproducibility (% Relative)	
	n-pentane	n-heptane	n-pentane	n-heptane
ACOSA[a]	11	12	21	14
Phillips[b]	6(4)	-	33(17)	-

[a] From triplicate analyses of an Athabasca bitumen and Lloydminster heavy oil sample by ten laboratories using n-pentane and four laboratories using n-heptane.

[b] From duplicate analyses by eight laboratories of a California and a Maya crude. The data generated by ASTM D2007 was not included. Numbers in parentheses were generated as a result of excluding data from one lab that used the Syncrude method and that reported results 5% higher than the other labs.

Table 11.2: Results of the Screening Design for Syncrude Analytical Method 5.1[5]

		Design columns								Unassigned factor columns							Asphaltenes (%)	
Trial	Ave.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	E_1	E_2	E_3	E_4	E_5	E_6	E_7	With fines	Corrected for fines
1	+	−	−	−	+	+	+	−	+	+	+	−	−	−	+	−	13.34	13.34
2	+	+	−	−	−	−	+	+	+	−	−	−	−	+	+	+	15.42	14.57
3	+	−	+	−	−	+	−	+	+	−	+	+	−	+	−	−	13.88	13.01
4	+	+	+	−	+	−	−	−	+	+	−	+	−	−	−	+	14.50	14.50
5	+	−	−	+	+	−	−	+	+	+	−	−	+	+	−	−	15.49	14.63
6	+	+	−	+	−	+	−	−	+	−	+	−	+	−	−	+	15.28	15.28
7	+	−	+	+	−	−	+	−	+	−	−	+	+	−	+	−	12.53	12.53
8	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	17.59	16.76
9	+	+	+	+	−	−	−	+	−	+	+	−	−	−	+	−	14.65	13.79
10	+	−	+	+	+	+	−	−	−	−	−	−	−	+	+	+	14.71	14.71
11	+	+	−	+	+	−	+	−	−	−	+	+	−	+	−	−	15.26	15.26
12	+	−	−	+	−	+	+	+	−	+	−	+	−	−	−	+	14.82	13.96
13	+	+	+	−	−	+	+	−	−	+	−	−	+	+	−	−	14.49	14.49
14	+	−	+	−	+	−	+	+	−	−	+	−	+	−	−	+	14.28	13.41
15	+	+	−	−	+	+	−	+	−	−	−	+	+	−	+	−	15.11	14.25
16	+	−	−	−	−	−	−	−	−	+	+	+	+	+	+	+	14.61	14.61
Ave	+	15.28	14.58	15.04	15.04	14.90	14.72	15.16	14.75	14.93	14.86	14.78	14.92	15.18	14.75	15.15		
Ave	−	14.21	14.92	14.45	14.46	14.59	14.78	14.34	14.74	14.56	14.63	14.71	14.57	14.31	14.75	14.34		
Diff		1.07	−0.34	0.59	0.58	0.31	−0.06	0.82	0.01	0.37	0.23	0.07	0.35	0.87	0.00	0.81		
Ave	+	14.86	14.15	14.62	14.61	14.48	14.29	14.30	14.32	14.51	14.43	14.36	14.50	14.76	14.32	14.73		
Ave	+	13.77	14.49	14.02	14.03	14.16	14.35	14.34	14.31	14.13	14.21	14.28	14.14	13.88	14.38	13.91		
Diff		1.08	−0.34	0.60	0.58	0.32	−0.06	−0.04	0.01	0.38	0.22	0.08	0.36	0.88	0.00	0.81		

With Fines

$s_{FE} = (1/7\ (0.37^2 + 0.23^2 + \ldots.\ 0.81^2))^{1/2}$

$[min]$ 95% confidence $= t_{95}\, s_{FE}$

$= 1.20$

$[min]$ 90% confidence $= t_{90}\, s_{FE}$

$= 0.96$

Corrected for Fines

$s_{FE} = (1/7\ (0.38^2 + 0.22^2 + \ldots.\ 0.81^2))^{1/2}$

$[min]$ 95% confidence $= t_{95}\, s_{FE}$

$= 1.19$

$[min]$ 90% confidence $= t_{90}\, s_{FE}$

$= 0.95$

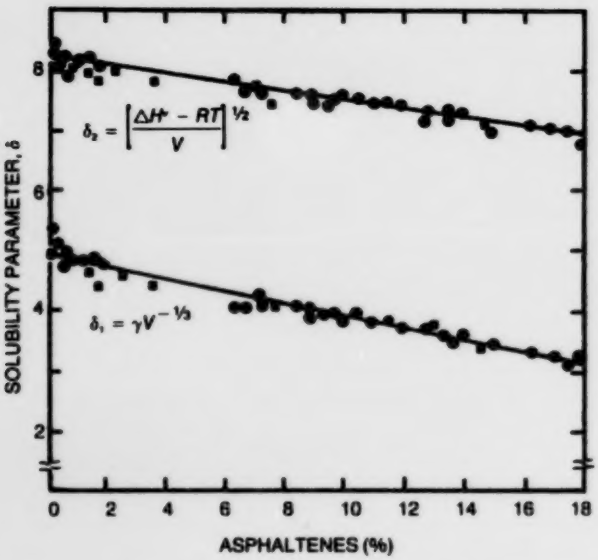

Figure 11.4: Relation of the Measured Asphaltene Content to Solubility Parameters (Reproduced from Fuel 1972, 52, 149-152, by permission of the publishers, Butterworth & Co. (Publishers) Ltd.)

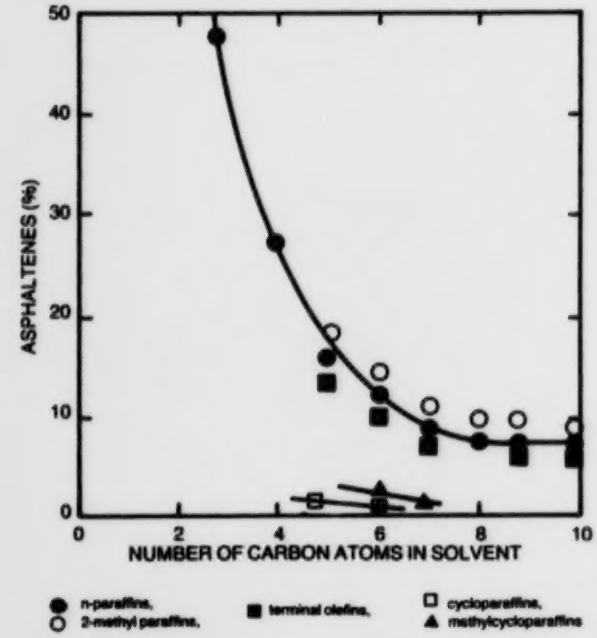

Figure 11.5: Relation of Measured Asphaltene Content to Carbon Atoms in Non-Aromatic Solvents (Reproduced from Fuel 1972, 52, 149- 152, by permission of the publishers, Butterworth & Co. (Publishers) Ltd.)

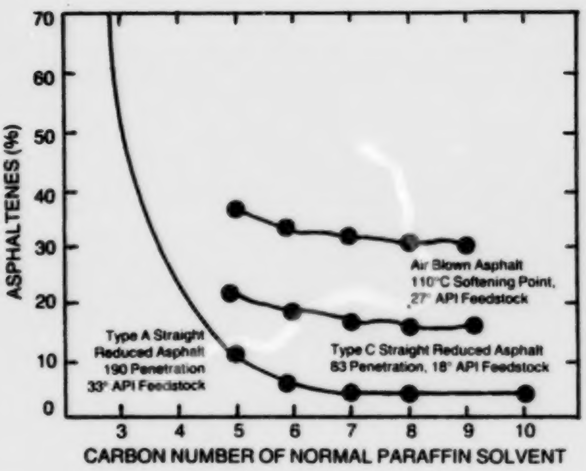

Figure 11.6: Effect of Solvent Carbon Number and Asphaltene Type on Percent Insolubles A solvent:asphalt ratio of 100:1 was used. (Reprinted with permission from Ind. Eng. Chem. Prod. Res. Dev. 1978, 17, 342-346. Copyright 1978, American Chemical Society.)

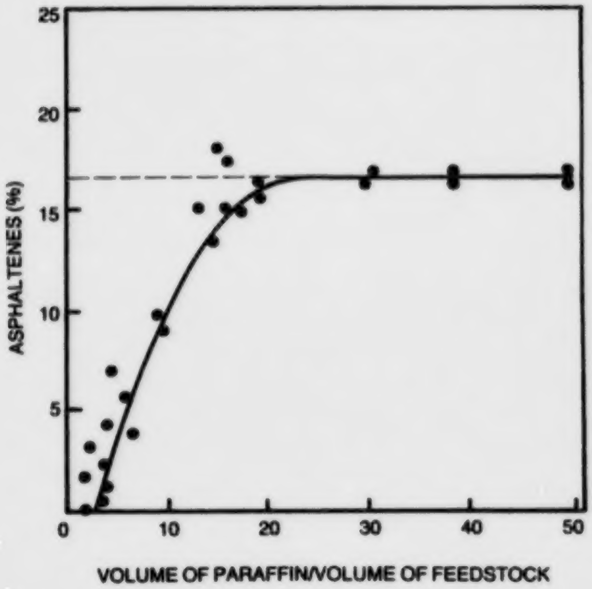

Figure 11.7: Relationship of Asphaltene Yield to Paraffin/Feedstock Ratio. Contact time was 16 hours. (Reproduced from Fuel 1972, 52, 149-152, by permission of the publishers, Butterworth & Co. (Publishers) Ltd.)

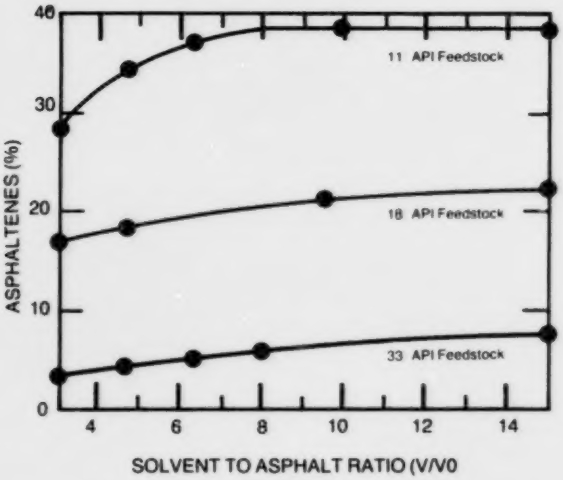

Figure 11.8: **Effect of Solvent Ratio on Percent of Pentane Asphaltenes from 90 Penetration Straight Reduced Asphalts** (Reprinted from Ind. Eng. Chem. Prod. Res. Dev. 1978, 17, 342-346. Copyright 1978, American Chemical Society.)

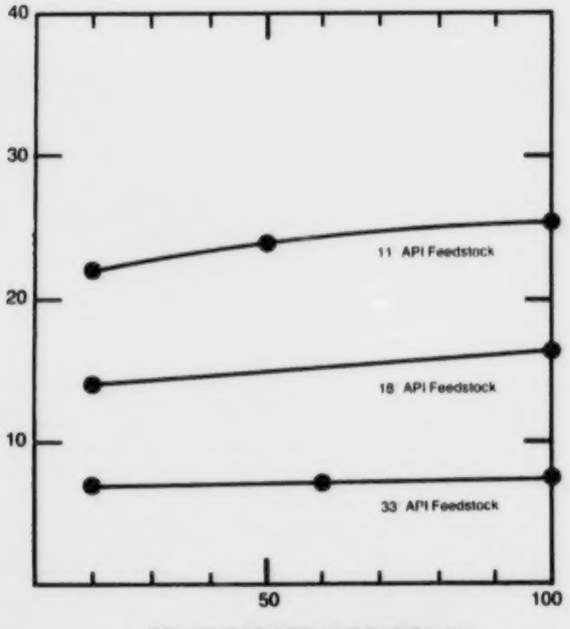

Figure 11.9: **Effect of Solvent Ratio on Percent of Heptane Asphaltenes from 90 Penetration Straight Reduced Asphalts** (Reprinted with permission from Ind. Eng. Chem. Prod. Res. Dev. 1978, 17, 342-346. Copyright 1978, American Chemical Society.)

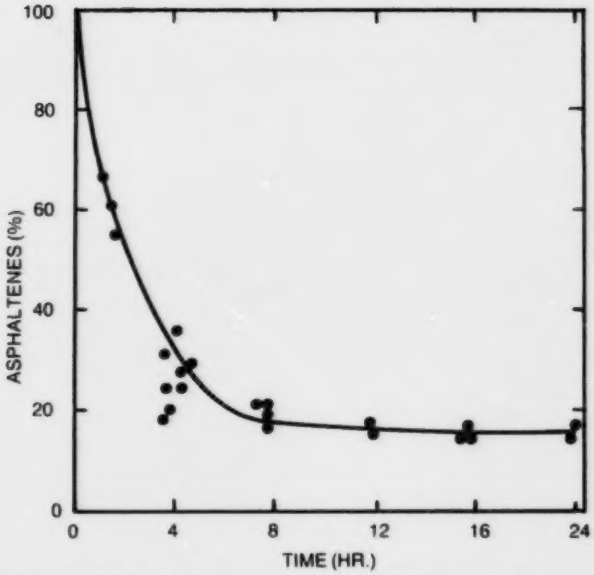

Figure 11.10: **Relationship of Asphaltene Yield to Feedstock/Paraffin Contact Time** Asphaltenes were precipitated from a mixture of 30 mL of pentane per gram of bitumen. (Reproduced from Fuel 1972, 52, 149-152, by permission of the publishers, Butterworth & Co. (Publishers) Ltd.)

Corbett and Petrossi reported reductions in asphaltenes precipitated from medium to light crudes as a result of using n-heptane, but they did not specify the conditions of precipitation.[4] Their results are summarized in Figure 11.6.

Results in Table 11.3 from the ACOSA cooperative study indicate that the relative precisions of data generated by precipitation with n-pentane and n-heptane are equal. Absolute precision is better with n-heptane but then the mean is also lower.

Solvent-Bitumen Ratio

The effect of varying the paraffin feedstock ratio on asphaltene yield is summarized in Figure 11.7 which was provided by Speight and co-workers at Exxon Research.[20] In this work the bitumen was not dispersed with solvent prior to precipitation. Speight stated that addition of an equal volume of benzene to the bitumen prior to precipitation with 40 volumes of pentane was equivalent to precipitation with 20 volumes of pentane alone, and so does not guarantee efficient separation of the asphaltenes.[20] A curve of asphaltene yield vs. pentane-to-bitumen ratio in which benzene or toluene was used as a dispersant would level out at a higher pentane-to-feedstock ratio than shown in Figure 11.7.

Corbett and Petrossi reported a similar levelling out for precipitation of asphaltenes with pentane and heptane from a variety of feedstocks.[4] No other details of the analysis were provided so a direct comparison of Figures 11.8 and 11.9 with Speight's results cannot be made.

Contact Time

Speight and co-workers concluded from studies of asphaltene precipitation from Athabasca bitumen with pentane, that precipitation should be allowed to proceed for 8 hours (Figure 11.10) to permit complete dissolution of resinous materials in the solvent.[20]

Correction for Solids in the Original Sample

Many bitumen and heavy oil samples contain levels of solids high enough to require a correction so that asphaltenes are reported on a solids-free basis. When a mathematical correction is made, it is assumed that the solids in the sample are retained with the asphaltenes. This has been confirmed experimentally (Table 11.2). Asphaltene values should be corrected by the equation:

$$\%\ \text{Asphaltenes}_{\text{corr}} = \frac{(\text{Wt. Asphaltenes}_{\text{meas}} - \text{Wt. Solids}) \times 100\%}{\text{Wt. Sample} - \text{Wt. Solids}} \quad (1)$$

Using this formula, the asphaltene content of a sample containing 0.5% inorganics and 15% precipitate would be reported as 14.6%. The need for correction increases with increasing levels of solids.

Removal of mineral matter prior to asphaltene precipitation and mathematical correction procedures are not included in many of the methods described in this review. Consequently, Syncrude Method 5.1, ASTM D2007, ASTM D4124, IP 143 and ASTM D3279 should be modified to acknowledge the presence of inorganic solids in most bitumen and heavy oil samples. UOP 99 already indicates that data should not be reported if inorganic solids are visible.

Analysts have two choices for determining the correction factor required because of solids in a test sample. A method has been described to determine the level of mineral matter in asphaltenes by infrared spectrometry.[7] Alternatively, the asphaltenes or a test portion of the original sample can be ashed and the ash value converted to a solids value by an appropriate factor. The conversion factor varies from 1.08 to 1.20[5-7] when ashing is conducted above 540°C. Its exact value depends on the source of the sample and the ashing temperature. Majid and Sparks described a low-temperature (400°C) ashing method that may provide a more accurate estimate of solids without the use of conversion factors.[10]

Sample Preparation

Payzant demonstrated that during extraction, the photo-oxidation of sulfur in alicyclic ring systems proceeds rapidly.[14] Wallace and Henry found that the apparent asphaltene content as defined by Syncrude Analytical Method 5.1 increased by an average of 0.9% for Athabasca bitumen but only 0.2% for Asphalt Ridge (Utah) bitumen[23] when the Soxhlet extraction was carried out for 24 hours instead of 3 hours. They also found that the average asphaltene content of bitumen extracted from oil sand in paper thimbles was 0.7% lower for Athabasca bitumen and 0.9% lower for Utah bitumen than for samples in wire thimbles. Corrections for residual solvent and solids were made in all cases.

Contribution of Sampling Error to Overall Error

Asphaltene determinations conducted on bitumen extracted from several-tonne lots of mined Athabasca oil sand showed that the uncertainty in a single asphaltene determination due to the variability of the bitumen between 1-kg increments of oil sand, is at least three times the magnitude of the sample preparation plus measurement uncertainly.[24] Little improvement in precision, therefore, results from replicate analysis of a test portion of bitumen if only one increment is collected from a bulk sample of oil sand.

Table 11.4: Variability in Asphaltene Content (Syncrude Analytical Method 5.1) in Single Cores[22]

Cold Lake bitumen		Athabasca bitumen			
Depth (m)	Asphaltene content (%)	Depth (m)	Asphaltene content (%) Neighboring samples		Mean
420	16.0	170	16.7	18.6	17.7
	15.6	177	19.9	18.4	19.2
	16.4	178	20.2	19.5	19.9
	-	186	20.6	20.0	20.3
	16.9	187	20.0	20.7	20.4
	-	196	20.6	21.2	20.9
430	17.2	201	21.0	20.2	20.6
	17.9	209	22.0	20.3	21.2
	16.8	215	18.9	20.1	19.5
	17.4	223	19.2	23.0	21.1
	-	231	20.5	19.5	20.0
	18.3				
	-				
440	18.4				
	-				
	-				
	18.3				
	18.8				
	-				
450	18.4				

Trends of increasing asphaltene content with increasing depth have been found in core samples taken from both the Athabasca and Cold Lake deposits.[22] The data in Table 11.4 describing the Athabasca core were collected in pairs, with members of each pair representing adjacent 5-cm intervals. The locations of the pairs were chosen randomly over the length of the core. The differences between the members of each pair exceeded the analytical repeatability in six of the eleven cases. Therefore, in deposit evaluations, sampling over the full core is necessary.

Other Factors

Most standard methods for asphaltene determinations do not provide adequate instructions regarding the addition of solvent to the bitumen or the washing of asphaltenes collected on the filter. Researchers at the Hydrocarbon Research Centre, University of Alberta, precipitate asphaltenes from bitumen dissolved in dichloromethane by slowly adding n-pentane using a buret while stirring.[12] This ensures a finely divided dry precipitate of asphaltenes and prevents oily asphaltenes from adhering to the walls of the container. Dichloromethane is used because it is easy to remove from the asphaltenes.

Researchers at both the Hydrocarbon Research Centre[12] and the National Research Council[9] have also found that Soxhlet extraction of asphaltenes removes long chain alkanes, hopanes and steranes that are occluded in the asphaltenes after washing on the filter. Most methods specify washing until the wash is colorless; for quantitive work this is suitable, but if characterizations are being conducted, Soxhlet extraction of the precipitate is recommended.

SUMMARY

Asphaltene analyses rarely provide the direct answer to a problem and so are usually done to support other data. As there is no definition of asphaltenes other than by solubility parameters, the method chosen should be one which is precise.

Precision is lost when no dispersing solvent is used unless the precipitation occurs under reflux or at elevated temperatures. For this reason ASTM D2007 and ASTM D893 which do not allow for dispersing solvents, are unsuitable for determining asphaltenes in bitumens and heavy oils. The possible effects of photo-oxidation and heat should also be considered when selecting a method. The method should also specify procedures for removal of solids or mathematical correction for solids, and should describe in detail the method of adding paraffin to the bitumen. Toluene can be substituted for benzene as a dispersing solvent without changing the percentage of the sample that precipitates.

The repeatability of asphaltene determinations in independent studies and in two cooperative studies generally fell within the limits as specified by ASTM standards. The reproducibility standard deviation from the cooperative studies was slightly higher due to the variations in methods used for each class of asphaltenes. Precision probably cannot be improved further if the method already provides data which fall on the plateaus of the solvent-bitumen ratio and contact time vs. asphaltenes curves as shown in Figures 11.7 and 11.10.

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Chapter 12: CARBON RESIDUE

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CARBON RESIDUE

DEFINITION

Carbon residue is the residue remaining after evaporation and pyrolysis of an oil under specified conditions. It indicates the relative coke-forming tendency of the oil under thermal degradation conditions.

SIGNIFICANCE

Coke is an undesirable byproduct from the primary upgrading of bitumens and heavy oils. It generally contains levels of metals and sulfur that prevent it from being used as a fuel without special combustion units. Higher yields of coke also imply lower yields of liquid products; therefore, crudes yielding lower levels of carbon residue are generally the more desirable feedstocks.

The tendency for carbon residue to increase with asphaltene content has been described in the preceding chapter. Carbon residue precursors are also found in the maltene fraction of bitumen. Bunger and Cogswell reported a Conradson carbon residue (CCR) of 8.2% for maltenes separated from Sunnyside (Utah) bitumen.[2] The original bitumen had an asphaltene content (precipitated from 40:1 pentane-to-sample) of 20.6% and a CCR value of 14.2%.

Similar results were obtained at the Alberta Research Council where Ramsbottom carbon residues (RCR) for Athabasca and Asphalt Ridge (Utah) maltenes were 5.4 and 6.8%.[7] The asphaltene content, determined by Syncrude Analytical Method 5.1, and RCR values for the Athabasca bitumen were 18.2 and 12.1%. The asphaltene and RCR values for the Asphalt Ridge bitumen were 8.8 and 9.0%.

METHODS

1. ASTM D524: Ramsbottom Carbon Residue (RCR) of Petroleum Products

1.1 Application

This method may be used for determining the carbon residue values of samples that are mobile enough to permit loading into a coking bulb.

1.2 Summary of the Method

A 0.5- to 1-g test sample weighed to 0.1 mg is injected into a weighed glass coking bulb which is placed in a metal furnace at 550°C. After a specified heating period, the bulb is removed from the furnace, cooled, and reweighed. Although the method acknowledges the possibility of ash-forming substances in the sample (specifically nitrates in diesel fuels), it does not provide for a mathematical correction for ash, nor does it consider the presence of inorganic solids.

1.3 Precision

Figure 12.1 illustrates the maximum allowable differences in measurements reported in ASTM D524 and in a recent report describing an ASTM interlaboratory

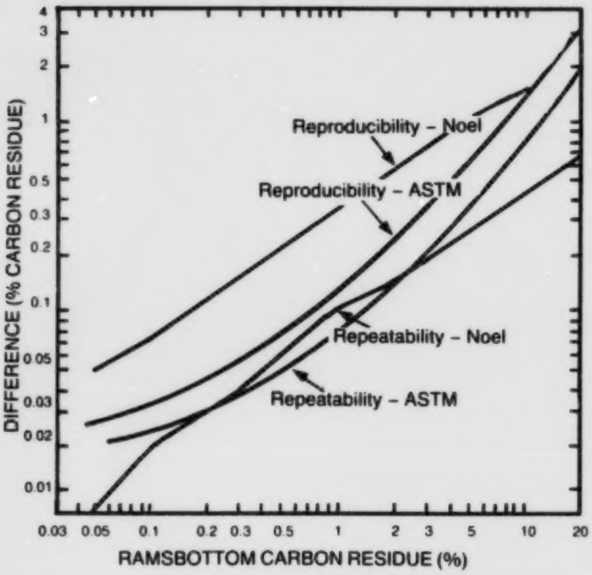

Figure 12.1: Precision Chart for ASTM D524 (RCR) An interlaboratory study to establish the Micro carbon residue test as an ASTM standard method, and comparisons between MCR and RCR provided the precision curves of Noel.[5] (Copyright ASTM. Reprinted with permission.)

study for successive tests by the same operator and by different laboratories. Other precision statements have been prepared from additional interlaboratory studies. These are given below:

	Repeatability (%)	Reproducibility (%)
ACOSA[a]	0.5	3.4
Phillips[b]	0.3	1.1
Wallace[c]	0.3	

[a] From triplicate analyses by four laboratories of an Athabasca bitumen (11.1% RCR) and a Lloydminster heavy oil (8.7% RCR).

[b] From duplicate analyses by five laboratories of a California heavy oil (9.0% RCR) and a Maya crude (10.7% RCR).[6]

[c] From the pooled standard deviation of analyses of eight pairs each of Athabasca and Asphalt Ridge bitumen samples. The samples within each pair were extracted by a specified method. The precision data, therefore, contain a level of uncertainty due to sample preparation.[8]

2. ASTM D189: Conradson Carbon Residue (CCR) of Petroleum Products and Syncrude Analytical Method 5.4: Determination of Conradson Carbon Residue of Bitumen and Distillation Residues

2.1 Application

This method is used to measure carbon residue when the sample is too viscous below 90°C to be loaded into a Ramsbottom coking bulb or when further testing of the residue is required.

2.2 Summary of the Method

A 5-g sample weighed to the nearest 5 mg is distilled and pyrolyzed in a tared porcelain or silica crucible containing two glass beads about 2.5 mm in diameter. Heat is applied by a Meker-type gas burner and vapors are ignited for specified time periods. The residue is cooled and weighed.

The Syncrude method describes a procedure for correcting the carbon residue value for percent ash. After the residue is weighed, it is burned in a muffle furnace at 750 ± 25°C until all carbonaceous material disappears. Then

$$\%\ \text{CCR} = \frac{(\text{Wt. of residue} - \text{Wt. of ash}) \times 100\%}{\text{Wt. of sample} - \text{Wt. of ash}} \qquad (1)$$

2.3 Precision

Figure 12.2 illustrates the maximum allowable differences reported in the ASTM standard between successive tests by the same operator and by different laboratories. Other estimates of precision are reported below for CCR values not corrected for ash.

	Repeatability %	Reproducibility (%)
ACOSA[a]	1.3	2.4
Phillips[b]	0.8	1.2
Noel[c]	15% relative	–
Shell[d]	1.6	–

[a] From triplicate analyses by ten laboratories of an Athabasca bitumen (13.2% CCR) and a Lloydminster heavy oil (10.4% CCR).

[b] From duplicate analyses by five laboratories of a California heavy oil blend (9.4% CCR) and a Maya crude (11.1% CCR).[6]

[c] From triplicate analyses of five 455+°C residues with a CCR content ranging from 5.5 to 24.2%.[4]

[d] From triplicate analyses of seven crudes with a mean CCR content of 11.1% and ranging from 7.4 to 13.8%.[7]

3. ASTM D4530: Micro Carbon Residue of Petroleum Products

3.1 Application

The Micro carbon residue (MCR) test, developed by Noel at Imperial Oil Ltd., is an alternative to the Conradson carbon test.[4] It yields the same numerical values but is more precise, less time-consuming, uses much smaller samples and allows simultaneous analysis of up to twelve test samples.

3.2 Summary of the Method

A 30- to 100-mg sample is heated at a prescribed rate and burned in a glass vial under a nitrogen blanket

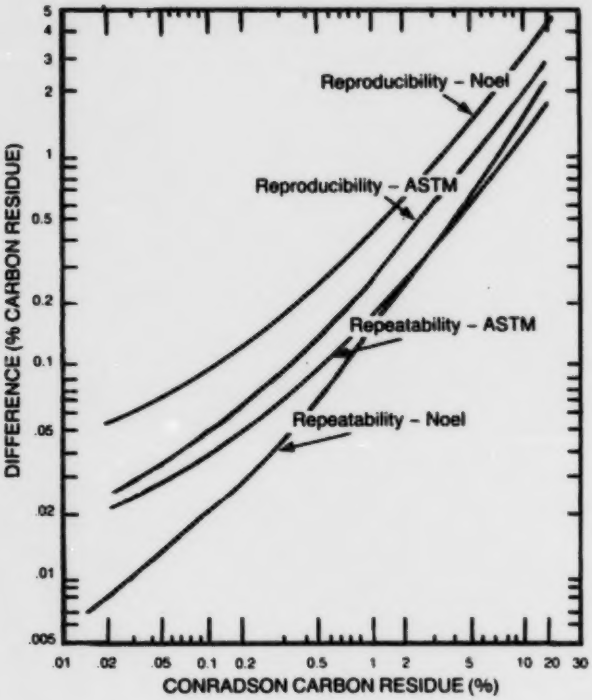

Figure 12.2: Precision Chart for ASTM D189 (CCR) An interlaboratory study to establish the Micro carbon residue test as an ASTM standard method, and comparisons between MCR and CCR provided the precision curves of Noel. (Copyright ASTM. Reprinted with permission.)

at 500°C ± 10°C for 20 minutes. The residue is weighed after cooling. Alcor Inc. of San Antonio, Texas, supplies a commercial unit which was used in studies leading to the development of the standard method.

3.3 Precision

In Noel's original work, triplicate analyses of five 455 + °C residues with 5.9 to 24.5% MCR indicated a repeatability of 0.9%.[4] Four replicate values for each resid were obtained in one run using a multisample MCR apparatus. Therefore repeatability of these data does not include between-run variations. Precision curves from the ASTM standard are provided in Figure 12.3. Repeatabilities determined by Shell Canada Ltd. for a variety of bitumen samples are included in this figure.

In the Phillips cooperative study, five laboratories conducted duplicate analyses of a California heavy oil (9.7% MCR) and a Maya crude (11.6% MCR). Estimates of repeatability and reproducibility from this study were 0.2 and 0.8%.

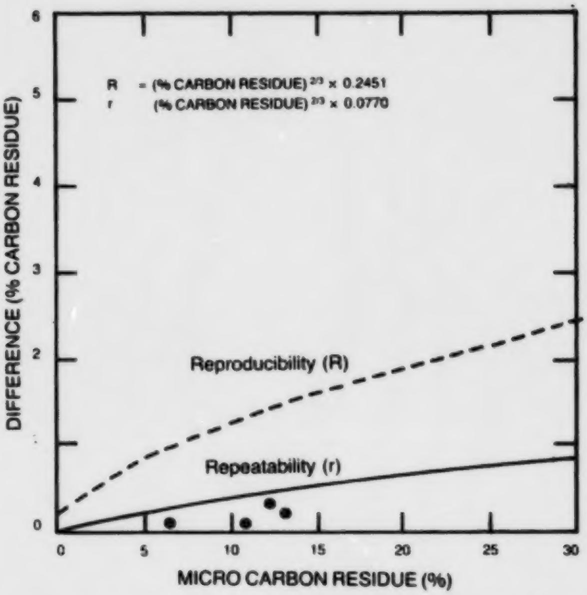

Figure 12.3: Precision Chart for ASTM D4530 (MCR) The data denoted by dots were provided by Shell Canada Ltd[3]. (Copyright ASTM. Reprinted with permission.)

DISCUSSION

Comparison of Analytical Data from Carbon Residue Methods

Numerous studies provide correlations among data from ASTM D189 (CCR), ASTM D524 (RCR) and ASTM D4530 (MCR). The ASTM correlations, given in Figure 12.4, show that ASTM D189 and ASTM D4530 provide equivalent data for levels of carbon residue up to 25%. This has been confirmed in other studies of crudes as reported in Table 12.1 and Figure 12.5. In Figure 12.5, a 1:1 correlation is apparent for carbon residue values up to 30%. For higher values, typical of asphalts and residues, the MCR test tends to provide slightly higher results.

Alcor Inc., manufacturer of a commercial MCR tester, provides three temperature programs to provide data equivalent to the CCR test.[1] Shell Canada's data in Table 12.2 indicates that program 2 and the base program gave equivalent results for samples with 7 to 13% carbon residue.[3] Supplementary program number 1 gave higher results by 2% relative. This difference was significant at the 95% level of confidence for all samples, but it is unlikely that this variation would contribute much to the reproducibility standard deviation in data between laboratories in an interlaboratory study.

Table 12.1: Comparison of RCR, CCR and MCR Data for Heavy Oils

	RCR (%)	MCR (%)	CCR (%)
Phillips[6]			
California heavy oil	9.0	9.8	9.4
Maya crude	10.7	11.7	11.1
Alberta Research Council[7]			
Wabasca	7.6	8.4	8.6
Fort Kent	9.0	9.9	9.8
Blackfoot	9.0	11.2	11.4
Battrum	10.0	11.0	11.0
Morgan	10.4	12.2	12.8
Westmin	11.2	12.2	12.4
Primrose	11.2	12.4	12.9
Lindbergh	11.2	12.5	13.0
Fort Kent	11.2	13.0	12.6
Cold Lake	11.3	12.5	13.2

Correlations for ARC Data	Standard Deviation Slope	Standard Deviation Intercept
%RCR = 0.851 %MCR + 0.399	0.10	1.17
%CCR = 1.055 %MCR + 0.393	0.08	0.96
%RCR = 0.776 %CCR + 1.071	0.10	1.23

Table 12.2: MCR Data from the Alcor MCR Tester[3] Each mean represents the average of nine determinations.

	MCR (%)					
	Base program-		Supplementary program #1-		Supplementary program #2-	
Sample	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
A	6.93	0.08	7.04	0.04	6.92	0.07
B	13.2	0.21	13.4	0.09	13.2	0.15
C	12.0	0.13	12.3	0.08	12.0	0.14
D	13.1	0.16	13.4	0.07	13.1	0.14

Table 12.3: Effect of Sample Cup Material on Percent Micro Carbon Residue[4] Triplicate 100 mg samples were pyrolyzed at 500°C.

Cup material	MCR (%)
Cold Lake 565+°C (CCR = 24.2%)	
Glass	24.6 ± 1.4
Aluminum	21.5 ± 0.7
Platinum	21.4 ± 0.4
Pembina 455+°C (CCR = 5.5%)	
Glass	5.5 ± 0.1
Platinum	4.1 ± 0.1

Table 12.4: Effect of Heating Rate up to 500°C on Percent Micro Carbon Residue[4] Triplicate tests were conducted at each condition on a Cold Lake 565+°C resid having a CCR content of 24.4%.

Test conditions			MCR (%)
Heating rate (C°/min)	Sample size (mg)	Container	
2	100	Glass cup	24.4 ± 1.0
15	100	Glass cup	24.6 ± 1.4
40	100	Glass cup	24.5 ± 1.0
10	5	Platinum cup	20.3 ± 1.0
80	5	Platinum cup	20.3 ± 1.1
160	5	Platinum cup	20.4 ± 1.1

Table 12.5: Effect of Air on the Coking Reaction[4] Triplicate 100 mg samples were pyrolyzed at 500°C.

	MCR (%)	
Sample	Air	Nitrogen
Cold Lake 565+°C (CCR = 24.2%)	29.5 ± 0.0	24.6 ± 1.4
Pembina 445+°C (CCR = 5.5%)	6.4 ± 0.6	5.5 ± 0.1

Other Factors

Noel developed the MCR test to reduce test sample size and improve precision while obtaining carbon residue values equivalent to CCR. To obtain equivalent data, he carried out extensive research into the reactions occurring during the test.[4] His findings are summarized below.

- Samples contained in glass crucibles yield more coke than those held in platinum or aluminum crucibles when all other conditions were fixed (Table 12.3). The effect of different types of glass on carbon residue has not been reported.
- Carbon residue is independent of heating rate when all other conditions are fixed (Table 12.4).
- The presence of oxygen in the early stages of coking increases coke yield (Table 12.5). In the CCR test, little oxygen is present in the burner flame whereas in the MCR test, it is necessary to blanket the samples with nitrogen to remove the oxygen. Failure to do so results in MCR values 20% higher than CCR values.
- Carbon residue decreases with increasing surface area-to-mass ratio.
- In the MCR test, pyrolysis occurs between 10 and 20 minutes after initiation of the test. Weight loss as a function of time for two resids is illustrated in Figure 12.6.

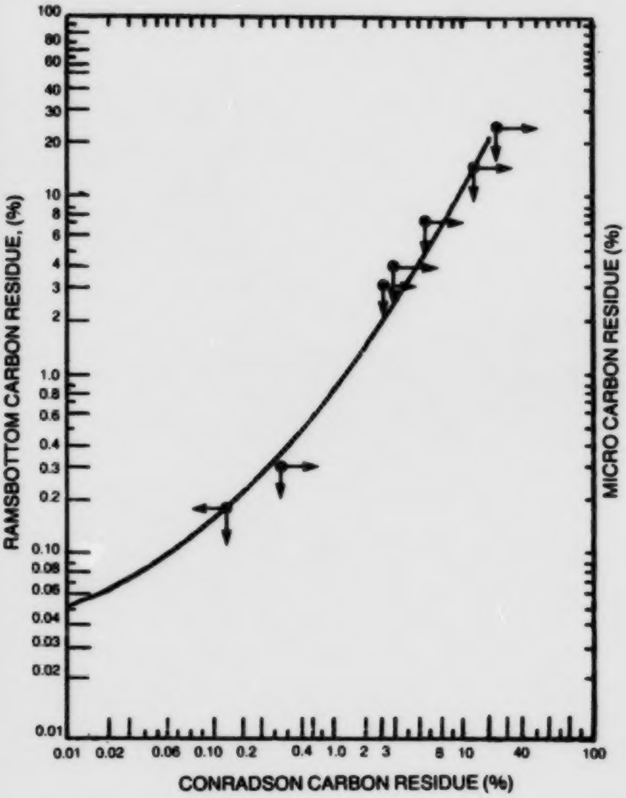

Figure 12.4: Correlations Between MCR, RCR and CCR The relationship between MCR (y) and CCR (x) is described by the line $y = 1.03x + 0.04$. The uncertainties of the slope and intercept are 0.02 and 0.23 respectively. (Copyright ASTM. Reprinted with permission.)

The effect of thimble type and extraction time on the level of asphaltenes in a solvent-extracted bitumen is described in the Chapter 11. Although asphaltenes are generally considered to be precursors of coke, researchers at the Alberta Research Council found thimble type and time did not significantly affect Ramsbottom Carbon Residue values.[8] The varying level of solids in the test sample was the greatest contributor to scatter in the carbon residue data. This error was eliminated by the mathematical correction for ash described in Syncrude Analytical Method 5.4. The correction for ash is related to the degree of volatilization of water of hydration from the solids, which is a function of ashing temperature. Ash produced by combustion at 540°C will be more similar to that in the carbon residue test than ash produced by combustion at 775°C. The systematic error as a result of ashing at the higher temperature probably will not exceed 0.1% absolute for materials containing less than 1% solids.

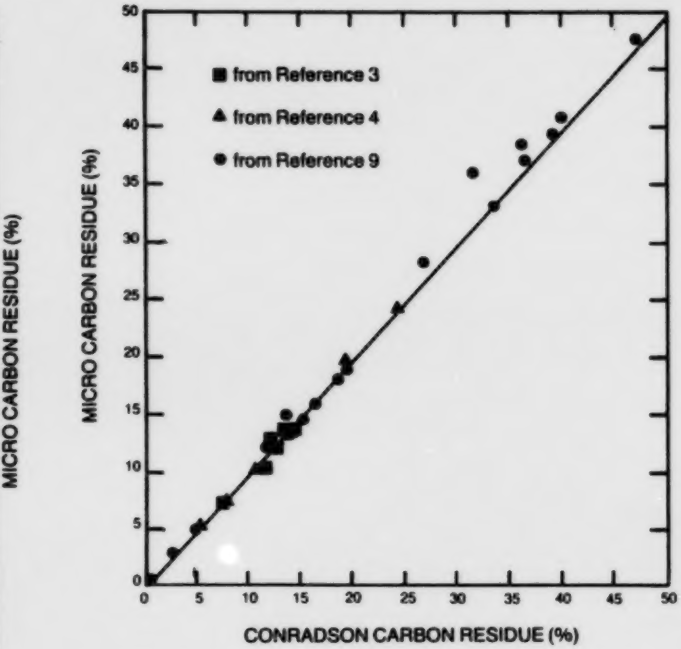

Figure 12.5: Correlation Between MCR and CCR The solid line denotes $y = x$.

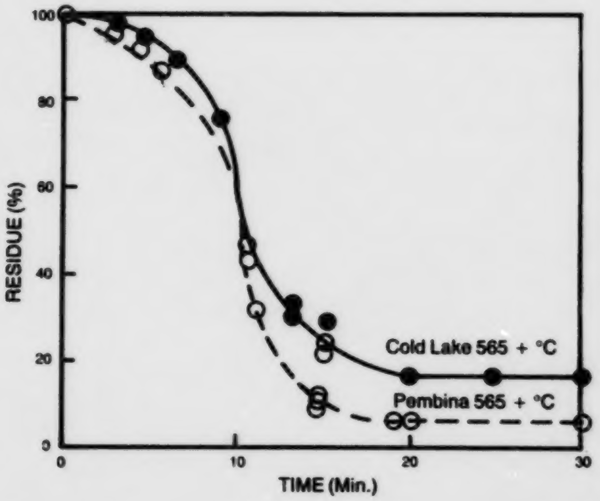

Figure 12.6: Rate of Pyrolysis During the MCR Test at 500°C[4]

Heating of heavy oils until they become fluid enough to permit collection of a test sample is not recommended because volatiles may be lost prior to weighing of the sample. A better strategy entails freezing with liquid nitrogen and then shattering the frozen sample into manageable pieces.

SUMMARY

Both the Phillips cooperative study and collaborative studies leading to the preparation of a standard MCR test, ASTM D4530, have illustrated the superior precision of the MCR method compared to ASTM D189. Increased subsampling errors when taking very small test portions are insignificant compared to the much greater control of conditions during the test.

Carbon residue data should be specified as Ramsbottom, Conradson or Micro carbon, and the result clearly identified as "corrected for ash" or "not corrected for ash".

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Chapter 13: ASH

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ASH

DEFINITION

Ash is the residue remaining after combustion of petroleum products. It is formed from organo-metallic components as well as inorganics such as clay and sand in the test sample. The relative contributions of these two sources to the level of ash is not determined. Ashing removes varying proportions of the water of hydration of solids and, depending upon the method, produces an oxidized or sulfated residue. Ash therefore is indicative of but is not a direct measure of the level of solids in the original sample.

SIGNIFICANCE

The level of ash in samples of bitumen and heavy oil is commonly determined for any of three reasons. First, ash may be used as an indicator of the quality of a crude. Crudes to be pipelined should contain low levels of ash as total solids and water must remain below 0.5% to meet pipeline specifications. In refineries, high levels of ash imply high levels of metals and solids such as sand and clay. Some metals affect catalysts while solids may form deposits in distillation columns and clog trays and lines.

Second, for analytical purposes, a measure of the level of ash is required to report carbon residue on an ash-free basis. Values for ash can also be converted to estimate the solids content which is used to correct measured values for asphaltenes, major elements and other properties. Organometallic and porphyrinic nickel and vanadium may contribute up to 0.1% ash in Athabasca bitumen. If these compounds contribute more than 50% to the total ash, a correction based upon the ash value need not be made.

Third, ash is sometimes determined in conjunction with the determination of metals in bitumen. There is still considerable controversy over the degree of volatilization of metals, vanadium in particular, during ashing. Analysts should err on the side of caution for this application and use a maximum temperature of 540°C. This topic is discussed in Chapter 14 which describes the determination of levels of nickel and vanadium. A low-temperature method to determine organics on solids, although not routinely used, is also discussed in this review.

METHODS

1. ASTM D482: Ash from Petroleum Products

1.1 Application

This method was designed for the determination of ash from fuels, crudes and other petroleum products.

1.2 Summary of the Method

A sample of sufficient size to produce up to 20 mg of ash is weighed to the nearest 0.1 mg into a platinum, silica or porcelain crucible which has previously been heated to 800°C, cooled and weighed. The crucible is then heated until the contents can be ignited with a flame. The temperature is maintained until burning ceases and the residue is heated at 775 ± 25°C until all carbonaceous material disappears. The crucible is weighed. Heating at 775°C for 20 minutes and weighing is repeated until successive weighings differ by less than 0.5 mg.

1.3 Precision

	Repeatability (%)	Reproducibility (%)
0.001 to 0.079%		
ASTM	0.003	0.005
Phillips[a]	0.011	0.025
0.080 to 0.180%		
ASTM	0.007	0.024
Phillips[b]	0.065	0.069

[a] From duplicate analyses by nine laboratories of a sample of Maya crude. The mean reported ash content was 0.05%.[6]

[b] From duplicate analyses by nine laboratories of a California crude. The mean reported ash content was 0.14%.[6]

2. ASTM D2415: Ash in Coal Tars and Pitches

2.1 Application

This method describes the determination of the ash content of tars and pitches.

2.2 Summary of the Method

A 10-g sample is weighed into a suitable crucible, volatilized and burned in a muffle furnace, on a hot plate or over a gas flame. The residue is then burned in a muffle furnace at 900°C. Ignition at 900°C is repeated until a constant weight is obtained.

2.3 Precision

Repeatability (%)	Reproducibility (%)
0.01	0.03

3. Syncrude Analytical Method 5.11: Wet Ashing of Gas Oil Samples

3.1 Application

This method is used to produce an ash prior to determining the nickel, vanadium and iron content of gas oil samples.

3.2 Summary of the Method

A 10-g sample is weighed into a 100-mL Vycor crucible. Ten millilitres of concentrated H_2SO_4 are added. The crucible is then heated on a hot plate. When the sample is charred, light from an infrared heat lamp is directed onto the sample SO_3 fumes are no longer visible. The crucible is covered with a watch glass and ashed at 540°C in a muffle furnace. The ash from this procedure is in a sulfated form.

3.3 Precision

Not established.

4. Alberta Research Council In-House Method[1]

4.1 Application

This method covers the determination of ash from bitumen and heavy oil.

4.2 Summary of the Method

A 10-g test sample is heated in a crucible on a hot plate to remove volatile matter. When no more fumes are visible, an infrared heat lamp is focussed on the sample initially from a distance of 10 cm. The distance is gradually reduced to less than 2 cm. The char remaining after this treatment is burned in a muffle furnace at 540°C to constant weight.

4.3 Precision

The repeatability, estimated from the pooled standard deviations of the data sets in Table 13.3, is 0.02%.

DISCUSSION

Dehydration of Test Samples

ASTM D2415, which describes the determination of ash from tars and pitches, recommends heating of a portion of the laboratory sample in an open container at 125 to 150°C to remove water. The dried sample can then be weighed and ashed. This is inappropriate for bitumens and heavy oils because they contain components which volatilize under such conditions. An ash level reported after water removal by this method would tend to be high because the volatile portion is lost before the test sample is weighed.

Centrifugation is another alternative if the solids which are removed with the water are added back into the sample before ashing.

Azeotropic distillation can also be used provided the test sample is mixed directly with the solvent in the boiling flask as opposed to being placed in an extraction thimble.

Fortunately, ash is often determined on products with low enough levels of water so that ash can be reported "as-received". If there is a problem with foaming and splattering during heating, leading to loss of sample, ASTM D482 recommends addition of a mixture of isopropyl alcohol and benzene (we prefer toluene for health reasons) prior to heating. Several strips of ashless filter paper are also placed in the mixture. Most of the water will have been removed by the time the strips begin to burn. Then, heating at higher rates can begin.

Ashing Temperature

Limited studies at the Alberta Research Council indicate that <37-micron solids, when dried at 110°C and then ashed at 540°C, lose 8 to 15% of their weight.[2] Ignasiak and co-workers reported a weight loss of 14% when clays from Athabasca oil sand were ashed at 900°C.[3] Loss of water of hydration therefore contributes more to the weight change during ashing than does a gain due to oxidation.

Majid and Sparks adopted a low-temperature ashing method to determine residual organic carbon levels in extracted oil sands.[5] They found that weight loss after ashing of the sands at 400°C for approximately 20 hours followed by equilibration with moisture at room temperature and 100% relative humidity could be attributed totally to removal of organic material. This ashing method may also be appropriate, although very time consuming, for determining solids in bitumen.

While developing the method, Majid and Sparks also found that mineral carbonates found in the solids are thermally stable at 400°C. It is not known if this holds true for all fines in bitumen. Even if it is, for routine determinations of solids in bitumen, quicker methods of ashing followed by a mathematical correction are probably sufficient.

In the ACOSA cooperative study, results obtained by ashing at temperatures above 750°C, an arbitrary cut point, were 0.03% lower than those obtained by ashing below 750°C for both Athabasca bitumen (0.47% ash) and Lloydminster heavy oil (0.12% ash). Chan found a slight decrease in ash values with increasing temperature for Athabasca bitumen.[1] He also studied a Cold Lake bitumen with 0.05% ash. This value was too low to permit identification of any trends. His data are reproduced in Table 13.1.

Table 13.1: Effect of Ashing Temperature on Reported Ash Content[1]

		Ash (%)		
		540°C	780°C	900°C
ASTM D2415	Cold Lake	0.07	0.05	0.07
	Athabasca	0.91	0.85	0.80
Syncrude wet-ashing	Cold Lake	0.06	0.05	0.10
	Athabasca	0.95	0.88	0.85
ARC adaptation of ASTM D2415	Cold Lake	0.04	0.06	0.06
	Athabasca	0.94	0.84	0.83

Table 13.2: Comparison of Precision Statements from the ACOSA and Phillips Cooperative Studies

	Repeatability (%)	Reproducibility (%)
ACOSA[a]		
Lloydminster heavy oil (0.12% ash)	0.06	0.12
Phillips[b]		
California heavy oil (0.14% ash)	0.06	0.08
Maya crude (0.05% ash)	0.02	0.04

[a] Triplicate analyses were conducted by twelve laboratories.

[b] Duplicate analyses were conducted by eleven laboratories.[1]

Other Factors

Given the general agreement that ashing temperature affects the reported ash value, one would expect that the ACOSA cooperative study in which temperatures ranging from 480 to 800°C were employed, should have given much poorer reproducibility statements than the Phillips study in which most labs followed ASTM D482 with the temperature fixed at 775°C. Comparison of the reproducibility for samples with equivalent levels of ash showed this to be true (Table 13.2).

Other factors, however, must also be considered. Charring and ignition should be carried out by increasing the temperature slowly to prevent a sudden and vigorous ignition of the sample which often produces large amounts of fly ash. An adequate supply of air is required to ensure complete combustion of organics and sometimes requires that the furnace door be left ajar.

Ashing should be carried out to constant weight. Chan and Wallace demonstrated that constant weight for a 540°C ash can be obtained in as little as 2 hours and as high as 5 hours.[1,7] Their data, shown in Table 13.3, indicate that combustion rates early in the ashing process varied considerably. These variations may have been due to the position and number of crucibles in the furnace, the varying amounts of oxygen available for combustion in different areas of the furnace, and variations in the degree of charring before the samples were placed in the muffle furnace.

Improper choice of crucibles can cause errors in estimates of ash values. Vycor and porcelain crucibles are suitable for ashing, whereas fused quartz crucibles tend to flake after severe heating. Corundum crucibles are too porous and will permit some of the sample to leak out of the crucible before it is ashed.

Collection of a test sample for determination of ash is an important step in an analysis, particularly for heavy oils and lighter bitumens where sedimentation is some-

Table 13.3: Rate of Weight Loss During Ashing[7]

	Ash at 540°C (%)				
Ashing time (hours)	**2**	**3**	**4**	**5**	**6**
Argentina heavy oil[a]	5.585 0.315	1.552 0.139	0.378 0.133	0.120 0.130	0.121 0.132
Wabasca cold-bailed bitumen[a]	0.126 0.146	0.124 0.139	0.116 0.123	0.114 0.127	0.114 0.126
Athabasca coker feed bitumen	0.633	0.630	0.620	0.622	0.624
Lloydminster fireflood[b] heavy oil	3.247 1.398	3.240 0.733	3.228 0.703	3.218 0.702	3.212 0.702
Malagasy heavy oil[a]	3.882 2.455	0.946 0.141	0.137 0.044	0.039 0.034	0.039 0.039
Malagasy heavy oil[a]	0.087 1.887	0.080 0.095	0.088 0.100	0.077 0.091	0.081 0.095
Athabasca coker feed bitumen[a]	6.502 4.987	1.874 1.047	1.043 1.045	1.033 1.032	1.034 1.028
Asphalt Ridge bitumen[b]	2.671 0.587	0.387 0.258	0.388 0.264	0.377 0.254	0.373 0.250

[a] Duplicate test portions from one sample.

[b] Different samples from one source (deposit).

times apparent. To determine if the solids in a 1-L jar of a commercially produced Athabasca bitumen could be evenly distributed by thorough mixing with an impeller-type mixer, Mahlow measured the ash content in a series of 5.6-mg and 43.9-mg test samples (Table 13.4).[4] Assuming the contribution of analytical error was insignificant compared to sample error, Visman's sampling constants (see Chapter 1) were estimated to be

$$A = \frac{43.925 \times 5.621}{43.925 - 5.621}(0.13^2 - 0.04^2) = 0.12 \text{ mg } \%^2$$

and

$$B = 0.04^2 - \frac{0.12}{43.925} = 0\%^2.$$

Therefore at, say, the 4 mg level, the variability in solids was approximately

$$\sqrt{\frac{A}{w} + B} = \sqrt{\frac{0.12}{4}} = 0.17\%$$

Visman's sampling constants suggest that the distribution of solids on the scale of one to five milligrams, the size of test sample often taken for microanalyses, does not contribute significantly to random error in carbon, hydrogen and nitrogen determinations (see Chapters 3 and 4).

SUMMARY

Ashing should be carried to constant weight rather than for a fixed time regardless of the temperature at which it is conducted. The temperature of ashing, the use of aids such as sulfuric acid, and whether or not the ash value is reported on an "as received" or a dry

Table 13.4: Variability in Ash Content of Crudes on the Micro-Scale[4]

	Series 1		Series 2	
	Test sample weight (mg)	**Ash (%)**	**Test sample weight (mg)**	**Ash (%)**
	6.115	0.82	35.010	0.51
	5.627	0.82	41.840	0.50
	5.200	0.60	45.029	0.47
	4.663	0.37	53.474	0.40
	6.015	0.54	41.995	0.50
	4.776	0.65	48.785	0.53
	5.277	0.66	41.034	0.48
	4.831	0.58	41.954	0.49
	7.011	0.60	46.207	0.42
	6.698	0.64	—	—
$\bar{x}$	5.621	0.63	43.925	0.48
s	—	0.13	—	0.04

basis should always be reported with the data. Ash values are not necessarily equivalent to solids content because of weight loss from the removal of water of hydration and mineral decomposition.

A low temperature ashing method has been developed to determine organic matter on extracted sands. It is probably too time-consuming for determining solids in bitumen.

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Chapter 14: NICKEL AND VANADIUM

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NICKEL AND VANADIUM

DEFINITION

Nickel and vanadium are metals which are incorporated in the organic structure of bitumens and heavy oils. No attempt will be made to differentiate between porphyrinic and nonporphyrinic forms.

SIGNIFICANCE

Levels of nickel and vanadium are considered when determining the origin of bitumens and heavy oils. Hodgson reported that oils formed in open-sea marine sediments have a relatively high level of nickel porphyrins compared to those formed in restricted marine bay environments where vanadyl porphyrins dominate.[17] He stated that for conventional oils, nickel porphyrins tend to dominate as sulfur levels decrease. Wallace and Carrigy confirmed this relationship (see Figure 6.1 in the chapter describing sulfur determinations) for a suite of bitumens and heavy oils from around the world.[45]

Hodgson also reported in a study of oils of Western Canada that the V/Ni ratio decreases with increasing maturation.[18] In independent studies of other oils, Hyden,[20] Ball,[4] and Al-Shahristani[2] reached the opposite conclusion while Demenkova[11] and Gilmanshin[14] concluded there is no correlation between V/Ni ratio and age.

Some metal porphyrins and organometallic compounds co-distill with heavy distillates during primary upgrading. During secondary upgrading these metal compounds, even at levels below 1 mg/kg, can modify the selectivity of zeolite-type cracking catalysts and cause an increase in the formation of coke and hydrogen at the expense of the more desirable liquid products.[6] They also rapidly deactivate catalytic cracking catalysts.[31]

Most of the metals however, concentrate in the coke residue produced during primary upgrading, thereby rendering the coke unuseable as a fuel source due to the risk of atmospheric pollution by the metal compounds in the stack gases.

METHODS

Techniques routinely used for the determination of nickel and vanadium include:

Atomic absorption spectroscopy (AAS)
Emission spectroscopy by inductively coupled plasma (ICP)
X-ray fluorescence (XRF)
Neutron activation analysis (NAA)
Colorimetric determinations

In this section, standard methods described in IP, Syncrude and UOP manuals will be summarized. Techniques which have not evolved into standard methods are addressed in the Discussion. The determination of iron is not discussed in detail because organic iron compounds are usually present in much lower concentrations than organic nickel and vanadium compounds.

1. UOP 800-79: Vanadium, Nickel and Iron in Petroleum Oils by Atomic Absorption Spectrophotometry

1.1 Application

This method covers the determination by atomic absorption spectrophotometry of vanadium at levels above 0.3 mg/kg and nickel and iron at levels above 0.1 mg/kg in petroleum oils.

1.2 Summary of the Method

A test sample weighing between 5 and 70 g is wet ashed in a Vycor beaker with fuming sulfuric acid, and the char is burned off in a muffle furnace at 540°C. The ash is dissolved in a sulfuric acid-hydrochloric acid mixture. Potassium chloride is added to suppress the formation of vanadium ions during measurement. Nickel is determined using an air-acetylene flame at a detector wavelength of 232 nm, and vanadium using a nitrous-oxide acetylene flame with a detector wavelength of 318.4 nm. Calibration solutions are prepared from high-purity nickel and vanadium.

1.3 Precision

	Repeatability
Nickel	
0.1 to 2 mg/kg	0.11 mg/kg
2 to 2000 mg/kg	5.7% relative
Vanadium	
0.2 to 2.5 mg/kg	0.16 mg/kg
2.5 to 2000 mg/kg	6.5% relative

2. Syncrude Analytical Method 5.11: Determination of Nickel, Iron and Vanadium in Gas Oil Samples by Inductively Coupled Argon Plasma Emission Spectroscopy Preceded by Wet Ashing

2.1 Application

This method describes the determination of nickel, iron and vanadium in gas oil at levels between 0.1 and 100 mg/kg in gas oils.

2.2 Summary of the Method

A 10-g sample of gas oil is charred with sulfuric acid in a Vycor crucible and ashed in a muffle furnace at 540°C. The ash is dissolved in hydrochloric acid and the solution analyzed by ICP. Calibration solutions are prepared from pure metals. Barium carbonate is employed as an internal standard for all sample and calibration solutions.

2.3 Precision

Not established for bitumens and heavy oils.

3. IP 288: Sodium, Nickel and Vanadium in Fuel Oils and Crude Oils by Atomic Absorption Spectroscopy

3.1 Application

This method describes the determination of sodium and nickel at levels above 1 mg/kg, and vanadium at levels above 10 mg/kg in crude and residual fuel oils.

3.2 Summary of the Method

The sample is diluted 1:10 with a mixture of 10 vol. % isopropyl alcohol and 90 vol. % white petroleum spirit. Nickel is measured using an air-acetylene flame and a detector setting of 352.5 nm. Vanadium is measured in a nitrous-oxide acetylene flame with a detector setting of 318.4 nm. Standard solutions of nickel 4-cyclohexylbutyrate and bis(1-phenyl-1,3-butanediono)oxovanadium are used for calibration.

3.3 Precision

	Repeatability	**Reproducibility**
Nickel	$0.375\ (\mathrm{Ni})^{0.801}$	$1.146\ (\mathrm{Ni})^{0.801}$
Vanadium	$0.150\ (\mathrm{V})^{0.976}$	$0.585\ (\mathrm{V})^{0.976}$

4. IP 285: Vanadium and Nickel in Petroleum Products – Spectrophotometric Method

4.1 Application

This method describes the determination of vanadium at levels above 10 mg/kg, and nickel at levels above 1 mg/kg in crude oils, fuel oils and their residues.

4.2 Summary of the Method

A sample not exceeding 30 g and elemental sulfur equal to one-tenth the sample weight are heated in a platinum crucible with a Bunsen burner until the sample ignites. The burner is then removed and the oil is allowed to burn. When the flame is extinguished, the sample is re-ignited and heated gently to maintain burning at a level which does not cause the crucible to become dull red. When burning ceases, the sample is ignited in a muffle furnace at 550°C. The residue is dissolved in sulfuric acid and diluted.

Color complexes of vanadium and nickel are prepared with sodium tungstate and dimethylglyoxime reagents and are compared spectrophotometrically with standard solutions of ammonium metavanadate and pure nickel.

4.3 Precision

	Repeatability	**Reproducibility**
Nickel	4 mg/kg	$2.24\ (\mathrm{Ni})^{0.5}$
Vanadium	$1.32\ (\mathrm{V})^{0.5}$	$4.16\ (\mathrm{V})^{0.5}$

DISCUSSION

Ashing of Samples Prior to Measurement

In the methods which require ashing prior to the measurement of metals contents, both sulfuric acid and elemental sulfur have been employed to prevent loss of volatile nickel and vanadium compounds. Considerable controversy exists over the degree of volatilization of organometallics during dry ashing. McCoy reported that most losses during dry ashing occur during initial burning of the sample rather than during final ignition.[29] Beach and Shewmaker,[5] and Scott, Collins and Hodgson,[38] identified the presence of both relatively volatile and nonvolative compounds of the same metal in a single sample. Therefore, if a crude containing both types of compounds is fractionated by distillation, dry ashing of the residuum might provide an accurate measure of nickel and vanadium whereas dry ashing of the distillate, which would contain most of the volatile metallic compounds would yield erroneously low results. Many researchers have proven this point by analysis of crude oils and their distillates.

Agazzi and co-workers showed that addition of elemental sulfur to the sample prevents loss of nickel and vanadium during ashing as effectively as sulfuric acid.[3] The sample data in Table 14.1 show that, up to 45% of the nickel and vanadium in the distillate fraction and approximately 20% in the residue was lost during dry ashing. The levels of nickel and vanadium in the sulfur they used for incineration were very low and so caused no appreciable errors in the analysis of the samples. In similar work, Shott and co-workers found that benzenesulfonic acid and sulfuric acid were equally effective in preventing loss of metals.[42] McCoy reported that vanadium sulfate decomposes at 700°C and Milner and co-workers reported a decomposition temperature of 750°C for nickel sulfate.[30]

Table 14.2: Comparison of Actual and Measured Metal Contents of a Spiked Sample Obtained by the Flame-Analyzed Wet Ashing Method[15]

	Actual (mg/kg)	Measured (mg/kg)	Deviation (% Relative)
Vanadium	34.8	32.5	6.6
	52.0	47.7	8.3
	48.1	44.2	8.1
	96.4	93.9	2.6
Nickel	26.1	23.1	11.5
	48.3	45.8	5.2
	47.8	46.1	3.6
	96.1	90.1	6.2

[a] The sample was a crude oil from Sooner Trend field, Oklahoma (1.1 mg/kg V; 0.4 mg/kg Ni), spiked with Conostan metallo-organic standards.

Grizzle and co-workers spiked crude oil samples of known nickel and vanadium content with Conostan organometallic standards and ashed the spiked sample with benzenesulfonic acid at a final temperature of 540°C.[15] The experimentally-determined metal contents of the spiked samples were approximately 6.5% lower than the theoretical contents (Table 14.2) but this deviation was only slightly greater than the uncertainty in the metal content of the standard. They concluded therefore that there was no appreciable loss of organometallics during wet ashing.

A detailed comparison of dry ashing and ashing with various additives was carried out by Ruana and co-workers for Boscan, Leona and Laguna heavy crude oils from Venezuela.[36] Their data in Table 14.3 suggest loss of vanadium during dry ashing of the Laguna crude but not from the Leona or Boscan crudes. The ammonium nitrate/sulfuric acid digestion reported in the table is essentially a modified Kjeldahl digestion adopted to minimize loss of metals and ashing time. No ash is produced; instead the organic material is destroyed and the metals dissolved in one step without final ignition in a furnace. Sample preparation time is usually reduced to 4 hours from an average of 6 hours for the other ashing methods. The major disadvantage of the ammonium nitrate/sulfuric acid digestion lies in the fact that the high content of

Table 14.1: Effect of Sulfur on Metal Loss During Incineration (Reprinted with permission from Anal. Chem. 1963, 35, 332-335. Copyright 1963, American Chemical Society.)

	Ni (mg/kg)[a]			V (mg/kg)[a]		
	Ordinary incineration	Incineration with S	Acid oxidation	Ordinary incineration	Incineration with S	Acid oxidation
Flash distillate PR-1	6.8	8.6	8.7	0.59	1.00	1.05
Flash distillate 105-1	11.3	16.0	16.1	2.9	3.43	3.44
Straight run residue 105-2	56	75	69	49	57	56

[a] Average of three to four determinations.

Table 14.3: Comparison of Various Ashing Methods for Heavy Crudes from Venezuela[3]

	Nickel (mg/kg)		Vanadium (mg/kg)	
	Colorimetric	A.A.	Colorimetric	A.A.
Boscan				
Dry Ashing	135.6	147.3	1175.5	1225.6
Benzenesulfonic Acid	151.2	153.4	1235.2	1185.1
Sulfur	152.2	153.3	1269.9	1269.3
Sulfuric Acid	130.2	137.7	1134.3	1119.9
Ammonium Nitrate/ Sulfuric Acid	—	153.2	—	1272.2
Leona				
Dry Ashing	33.1	33.2	115.6	118.9
Benzenesulfonic Acid	33.3	35.6	114.2	100.5
Sulfur	32.8	33.8	113.7	124.4
Sulfuric Acid	31.6	33.6	112.1	102.0
Ammonium Nitrate/ Sulfuric Acid	—	35.4	—	116.1
Laguna				
Dry Ashing	54.1	57.7	338.6	385.4
Benzenesulfonic Acid	54.9	56.5	433.8	433.7
Sulfur	55.6	56.3	433.0	430.8
Sulfuric Acid	57.9	57.7	447.6	449.4
Ammonium Nitrate/ Sulfuric Acid	—	58.7	—	453.8

ammonium salts in the final solution precludes the use of colorimetric methods for determining nickel and vanadium.

The Kjeldahl digestion was Ruana's method of choice for several reasons. In all other digestion methods, the presence of water leads to splattering of the sample during heating. Addition of isopropanol/toluene to azeotropically distill the water can seriously prolong ashing time. Also when numerous samples are ignited simultaneously in a muffle furnace, any fly ash (light carbon ash) which is produced may contain some metals and contaminate other samples. A further complication involves the need to redissolve the ashed metals. McCoy stated that the composition of the crucible may introduce errors into the determination of metals as platinum can be attacked by nickel in the presence of carbonaceous materials and vanadium fuses to porcelain to some extent.[29] Hofstader reported contamination of 500-mL Vycor crucibles with nickel in the 20-200 ng range after ashing samples containing parts per million nickel.[19]

When ashing with sulfur all of the sulfur added to the sample should be reacted by the time ignition is complete. If it is not, the ashing must be repeated using less sulfur. Methods which involve addition of sulfuric acid or benzenesulfonic acid are relatively hazardous to perform because of the nature and volume of the reagents required.

Direct Dilution of Test Samples

The problems associated with ashing of crude oils and dissolving of ashed metals prior to measurement have led analysts to search for simpler and less time-consuming sample preparation techniques. Method IP 288, which describes analysis by atomic absorption of a sample diluted in an appropriate organic solvent, is one alternative. This approach, however, has many shortcomings. Significant errors can occur if the viscosities of the sample and the standards used to prepare the calibration curve are not similar. Nemuki and co-workers prepared mixtures with widely varying ratios of lube oil in 10:30:60 methanol: toluene: methylisobutylketone but identical nickel and vanadium contents (presumably by addition of organometallic standards).[32] Although the range in viscosities of these mixtures was not identified, it is obvious from Figures 14.1 and 14.2 that the sample-to-solvent ratio should be very low if the standard calibration curve is derived from standards in pure solvent. Nemuki concluded that direct dilution is not appropriate for the determination of metals in crude oil.

As a first approximation only, the Poiseulle equation

$$Q = \frac{Pr^4}{8\eta l} \tag{1}$$

in which the flow rate, Q, of a solution through a capillary is seen to be inversely proportional to its viscosity, η, can be used to explain the reduced flow of a sample to the burner and hence the reduced atomic absorption signal.[21] In addition to Nemuki's study, other researchers have studied the effect of viscosity on readings for various metals by adding lube oils to organic solutions and ethylene glycol or glycerol to aqueous solutions of metals.[7,10]

A difference in viscosities between sample and standard solutions also contributes to a difference in the mean droplet diameter of liquid entering the flame, which is described by the following equation:

$$D_o = \frac{585\ (\gamma/\rho)^{0.5}}{(V_g - V_l)} + 597\ (\eta/\gamma\rho^{0.5})^{0.45}\ 1000(Q_l/Q_g)^{1.5} \tag{2}$$

where:

D_o = the mean droplet diameter
V_g = gas flow velocity
V_l = liquid flow velocity
η = solvent viscosity
γ = solvent surface tension
ρ = solvent density
Q_g = gas flow rate and
Q_l = liquid flow rate

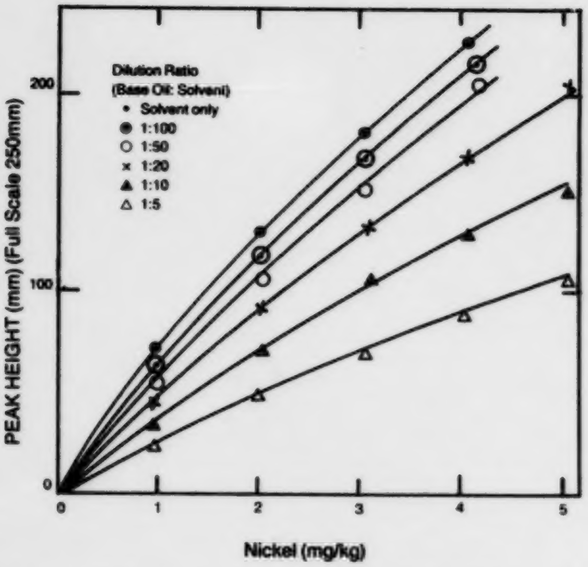


Figure 14.1: Sensitivity Curves for Nickel in the Direct Dilution-Atomic Absorption Method[32]

Operating Conditions

Instrument	Hitachi 208
Air	13L/min
Acetylene	1.75L/min
Burner	1 slot
Attenuation	10mV
Wavelength	232.0nm

If the average diameter of the droplets entering the burner is large, desolvation of the droplet takes longer and the atoms of metal may remain solvated in the flame and thus not be measured. The desolvation rate of a droplet in a flame may be expressed by

$$D_t^2 = D_o^2 - kt \qquad (3)$$

where:

D_t = droplet diameter after time t in the flame
D_o = initial droplet diameter, and
k = desolvation rate constant for each solvent.[8,9,16]

The rate constant k is defined by the expression

$$k = \frac{8\lambda M}{C_p\rho_l}\ln\left[\frac{1 + C_p(T_g - T_s) + \beta Q}{H_v}\right] \qquad (4)$$

where:

λ = thermal conductivity of the vapor surrounding a droplet
C_p = heat capacity of the vapor
ρ_l = density of the solvent
M = molecular weight of the solvent
T_g = temperature of the flame
T_s = boiling point of the solvent
β = ratio of the amount of oxygen present to that needed for stoichiometric combustion
Q = heat of combustion of the solvent and
H_v = heat of vaporization of the solvent.

λ, C_p and T_g would all be affected by the ratio of sample to solvent in the test samples. Although the effect of viscosity on mean droplet size and desolvation rate may be minor compared to its effect on volumetric flow rate, these ideas are presented to illustrate that a mathematical correction for viscosity effects of a signal is not easily calculated.

The effect of a difference in viscosity between a test sample and standard solution can be avoided either by careful viscosity matching of standards and samples or by using a method of standard addition. Grizzle and co-workers found, however, that standard addition does not overcome problems such as carbon deposition on the burner head, clogging of the capillary with undissolved solids and precipitated petroleum fractions if the solvent is unsuitable, and temperature fluctuations in the flame caused by aspiration of water in the sample.[15] Grizzle analyzed twenty-two test samples by standard addition of NBS material GM-5 (a residual oil with a relative density of 1.001 at 15°C/15°C and standard metal contents

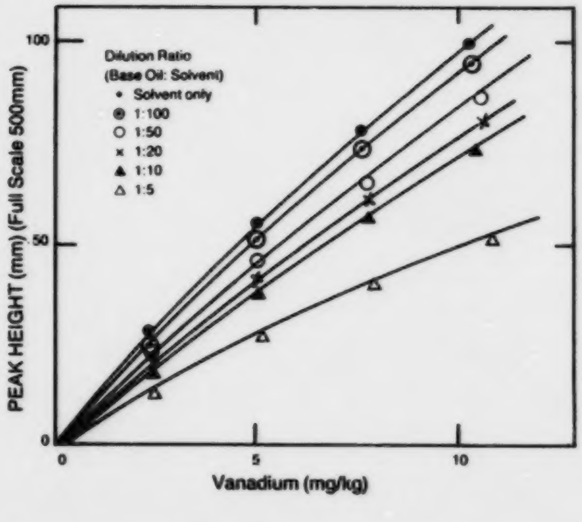


Figure 14.2: Sensitivity Curves for Vanadium in the Direct Dilution-Atomic Absorption Method[32]

Operating Conditions

Instrument	Hitachi 208
Air	9L/min
Acetylene	6L/min
Burner	1 slot
Attenuation	5mV
Wavelength	218.4nm

of 79.0 ± 1.2 mg/kg V and 93.3 ± 1.2 mg/kg Ni) and obtained mean results of 82.0 mg/kg V and 119.8 mg/kg Ni. Grizzle used Conostan organometallics as internal standards. He found repeatabilities of 38.2 and 54.6 mg/kg for nickel and vanadium. He attributed this lack of repeatability to the actual measurement step rather than heterogeneity of the sample because measurements of the same dilutions were often not similar. In contrast to the imprecise and inaccurate dilution-flame analysis data, Grizzle found 79.9 mg/kg V and 87.4 mg/kg Ni by wet ashing-flame analysis. Repeatabilities by this method were 12.45 mg/kg V and 10.19 mg/kg Ni. Grizzle then compared the dilution and wet ash methods of sample preparation for analysis of petroleum samples and again found the former to be imprecise (Table 14.4). The direct dilution method also tended to give relatively high results.

Table 14.5: Nickel in Petroleum Residues Obtained with Different AAS Methods[41] Each mean was calculated from three measurements.

	Nickel (mg/kg)		
	Ashing	Dilution with xylene	Dilution with MIBK
Assam crude residue (530°C +)	3.5 ± 0.3	8.4 ± 1.5	7.2 ± 2.5
Gujarat crude residue (500°C +)	56.8 ± 2.1	67.3 ± 3.1	63.6 ± 5.2
Bombay High residue (500°C +)	7.8 ± 0.6	16.1 ± 2.8	14.2 ± 3.4

Sharma and Singh encountered similar problems in their comparison of methods for determining nickel in petroleum resids.[41] Values in Table 14.5 obtained by dilution were not only less precise but larger than those obtained from wet-ashed samples. Sharma and Singh concluded that the difference was due to a matrix effect caused by the fact that the organometallics in the residua were different compounds than those in the standards. Leonard and Swindall showed that the nickel compounds having nickel-oxygen bonds tend to give a peak absorbance higher in the flame than other types of compounds (Figure 14.3).[26] They attributed this observation to the tendency of the former to form nickel oxides in the flame which do not readily dissociate to free metal atoms. Vavrecka and co-workers illustrated the potential magnitude of this "matrix" effect by comparing the absorbance of bis-(1-phenyl-1,3-butanediono)oxovanadium and the nickel (II) salt of cyclohexylbutyric acid with the same levels of vanadium and nickel in the form of porphyrin structures.[44] The effect of the variations in the calibration curves on the estimates of nickel and vanadium is shown in Table 14.6. Vavrecka concluded that the most suitable standards for direct aspiration methods are metal porphyrins. His paper describes a procedure for their preparation.

Lang, Sebor and co-workers compared the slopes of calibration curves for eight nickel compounds dissolved in xylene and found the slopes to differ markedly in both nitrous oxide-acetylene (Figure 14.4) and air-acetylene flames.[24] The variability in analytical data due to the use of these different standard compounds for calibration is given in Tables 14.7.

They also carried out similar studies for vanadium in which an additional factor, the use of potassium as an ion suppressant was examined.[25,30] Since vanadium is easily ionized at the temperature of the nitrous oxide-acetylene flame and only metals in the atomic state are measured in an AA flame, the addition of potassium should increase the sensitivity of the measurements (the slope of the absorbance vs. concentration curve). Figure

Table 14.4: Vanadium and Nickel Concentrations in Selected Crude Oils[a] Determined by Flame-Analyzed Dilution and Flame-Analyzed Wet Ashing Methods[15]

	Vanadium (mg/kg)		Nickel (mg/kg)	
	Dilution	Wet ash	Dilution	Wet ash
Village Mills East, Texas[b]	2.9 ± 5.0	0.1 ± 0.0	0.4 ± 0.2	0.5 ± 0.0
Village Mills East, Texas[b]	2.6 ± 4.6	0.1 ± 0.0	3.5 ± 4.1	0.6 ± 0.0
Village Mills East, Texas[b]	3.0 ± 5.2	0.2 ± 0.1	3.8 ± 4.7	0.6 ± 0.0
Kismet Northwest, Kansas	17.4 ± 6.2	17.0 ± 0.1	7.9 ± 2.7	6.6 ± 0.1
Earlsboro, Oklahoma	6.5 ± 6.9	2.4 ± 0.1	7.7 ± 3.4	1.4 ± 0.1
Ship Shoal, Louisiana	0.2 ± 0.4	0.4 ± 0.1	3.0 ± 2.6	0.9 ± 0.0
Sooner Trend, Oklahoma	4.2 ± 5.0	1.1 ± 0.1	7.3 ± 9.5	0.4 ± 0.1
Sunoco Felda, Florida	42.0	45.5 ± 2.5	70.5	45.9 ± 1.6
Gillisburg, Mississippi	1.2 ± 0.4	0.1 ± 0.1	4.7 ± 2.1	0.4 ± 0.4

[a] Samples were chosen from a group of more than 230 crude oils and residua (crude oil topped to 420°C) which were analyzed for vanadium and nickel by either or both of the two sample preparation techniques.

[b] Texas samples are from the same field but different wells representing different producing zones.

Table 14.6: Vanadium and Nickel Contents in Some Oil Samples (Reprinted with permission from Riv. Combust. 1975, 29, 375-379.)

	Vanadium (mg/kg)		Nickel (mg/kg)	
	A	B	A	B
Asphalt from Romanashkino oil	413	573	108	128
Asphaltene from Romanashkino oil	869	1206	239	281
Asphaltenic extract C_6H_6-CH_3OH (1:1 vol)	564	816	95	117
Residue after extraction of asphaltenes with C_6H_6-CH_3OH (1:1 vol)	1190	1556	358	415
Residue after extraction of asphaltenes with C_4H_9OH	1027	1374	300	350

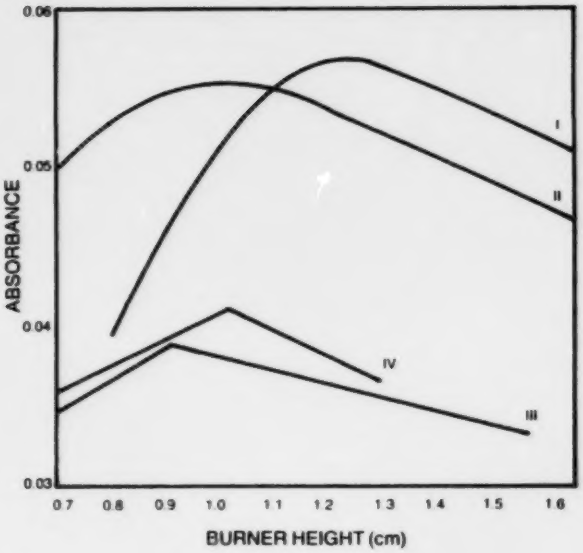
A = metalloporphyrin calibration curve

B = commercial standard calibration curve

14.5 provides calibration curves of three vanadium standards in xylene with and without addition of potassium. The figure illustrates the different slopes for the three different standard compounds but also indicates that potassium acts as an ion suppressant for one standard, vanadyl tetraphenylporphyrin (VOTPP), has no effect on the Conostan standard, and weakens the signal for a third standard, vanado benzoylacetonate (VOBA). Lang suggested that potassium forms complexes of different thermal stabilities with vanadium in the Conostan and VOBA standards and that the ease of release of vanadium from these complexes determines the magnitude of the vanadium atomic absorption signal.

Table 14.8 shows that the vanadium content determined in petroleum samples depends on the standard used to prepare the calibration curve. In the absence of potassium, use of VOTPP for calibration (curve 2 in Figure 14.5) yielded the lowest results and the Conostan standard curve (curve 6 in Figure 14.5) gave the highest results. When potassium was added to the samples, the results using the VOTPP + K calibration curve were similar to those when no potassium was used in the samples and standards. This suggests that the effect of potassium on the samples in this study was similar to its effect on VOTPP. Use of the VOBA + K and Conostan + K curves resulted in significant increases in the measured vanadium content.

When these results were extended to the method of standard addition (Table 14.9), addition of VOTPP to a solution with a known concentration of VOBA yielded a low estimate of the vanadium in the VOBA solution. Addition of VOBA to a known solution of VOTPP led to a positive error. The standard addition technique for real samples was more successful because metals in these samples were probably partially porphyrinic and partially nonporphyrinic and so did not provide the extremes in absorption characteristics evident in pure compounds.



I, nickel cyclohexylbutyrate containing 10 μg/mL of nickel; II, $Ni[P(C_2H_5)_2C_6H_5]_2Cl_2$ containing 9.6 μg/mL of nickel; III, $NiP(C_6H_5)_3C_5H_5Cl$ containing 7.0 μg/mL of nickel; and IV, $NiP(C_2H_5)_3C_5H_5GeCl_3$ containing 7.4 μg/mL of nickel

Figure 14.3: Effect of Burner Height on Absorbance for Organonickel Compound in 30:70 Chloroform:MIBK (Reprinted with permission from Analyst 1973, 98, 133-136.)

In subsequent work, Lang and Sebor demonstrated conclusively that addition of ion suppressants such as potassium or sodium for determination of vanadium in xylene solutions causes varying degrees of error.[25] The magnitude of the error depended upon the form of the suppressor compound (see Figure 14.6). In other studies, potassium cyclohexanebutyrate added to VOTPP enhanced the signal but potassium Conostan standard weakened the signal. Similar variations were found for the addition of potassium to petroleum samples (Figure 14.7). The weaker signal for "aged" standard solutions of vanadium (Figure 14.6) was attributed to the formation of organic "conglomerates" in solution which vaporize slowly in the flame thereby increasing the probability of conversion of vanadium to a stable carbide rather than atomic vanadium.

In the following section describing flameless atomic absorption, the role of halogens in eliminating matrix effects for nickel and vanadium compounds is described. Although researchers have found that addition of halogen eliminates matrix effects for the determination of lead in gasoline[22], Sebor and Lang found that addition of

Table 14.7: Nickel Contents in Petroleum Samples Determined in Air-Acetylene and Nitrous Oxide-Acetylene Flames (Reprinted with permission from Anal. Chim. Acta 1979, 84, 299-305.)

	Nickel (mg/kg)							
Sample[a]	**NiTPP[b]**	**NiCHB**	**NiAA**	**NiBA**	**NiNaph**	**NiMTAA**	**NiDTAA**	**NiCON**
Air-acetylene flame (Calibration curve technique)								
1	33.8	36.2	33.8	3.8	36.2	44.9	44.9	36.2
2	10.9	11.3	10.9	10.9	11.3	13.2	13.2	11.3
3	41.8	45.9	41.8	41.8	45.9	55.6	55.6	45.9
4	27.5	29.3	27.5	27.5	29.3	35.4	35.4	29.3
5	17.9	18.8	17.9	17.9	18.8	22.6	22.6	18.8
6	40.7	44.0	40.7	40.7	44.0	53.4	53.4	44.0
7	50.1	54.4	50.1	50.1	54.4	65.4	65.4	54.4
8	117.1	127.6	117.1	117.1	127.6	160.4	160.4	127.6
Air-acetylene flame (Standard addition technique)								
1	47.9	46.1	43.3	44.2	47.0	73.7	65.0	50.7
2	14.2	12.8	14.3	13.5	13.6	18.1	17.8	13.1
3	53.8	44.9	49.3	51.5	55.5	72.2	70.2	53.5
4	31.9	32.2	31.0	34.4	34.9	44.4	40.0	33.1
5	22.7	24.0	20.9	15.7	17.7	32.7	31.2	26.1
6	48.9	47.2	47.2	46.1	50.6	70.4	71.0	48.3
7	62.3	52.1	60.8	55.7	65.9	95.8	70.1	67.9
8	129.9	139.0	—	129.9	144.1	187.0	179.2	132.5
Nitrous oxide-acetylene flame (Calibration curve technique)								
1	35.3	39.8	35.3	32.0	38.6	47.1	47.1	42.2
2	10.2	11.8	10.2	10.6	11.3	13.2	13.2	12.5
3	42.7	48.7	42.7	44.9	47.3	58.9	58.9	51.7
4	25.8	29.5	25.8	27.1	28.6	34.1	34.1	31.0
5	16.2	18.6	16.2	17.2	18.1	21.1	21.1	19.5
6	41.6	47.3	41.6	43.8	46.0	55.8	55.8	50.1
7	51.6	59.5	51.6	54.1	54.8	70.3	70.3	62.5
8	124.7	144.6	124.7	132.8	140.0	175.0	175.0	154.0

[a] Sample numbers correspond to:

1. a deasphalted sample from Romashkino vacuum residuum (U.S.S.R.), 43.5 mg/kg Ni;
2. a deasphalted sample from Kuwait vacuum residuum, 13.8 mg/kg Ni;
3. Karathoug crude oil (Syria), 50.0 mg/kg Ni;
4. Morgan crude oil (Egypt), 28.1 mg/kg Ni;
5. a hydrogenated atmospheric residuum from Romashkino crude oil, 18.6 mg/kg Ni;
6. an atmospheric residuum from Romashkino crude oil, 51.3 mg/kg Ni
7. a Romashkino propane asphalt, 59.5 mg/kg Ni;
8. a Saratoff propane asphalt (U.S.S.R.) 130.5 mg/kg Ni.

Referee determinations of nickel were obtained by wet ashing in p-xylenesulfonic acid followed by AA.

[b] **Standard compounds were:**
NiTPP-Nickel tetraphenylporphyrin
NiCHB-Nickel cyclohexanebutyrate
NiAA-Nickel acetylacetonate
NiBA-Nickel benzoylacetonate
NiNaph-Nickel naphthenate
NiMTAA-Nickel monothioacetylacetonate
NiDTAA-Nickel dithioacetylacetonate
NiCON-Conostan Nickel Standard

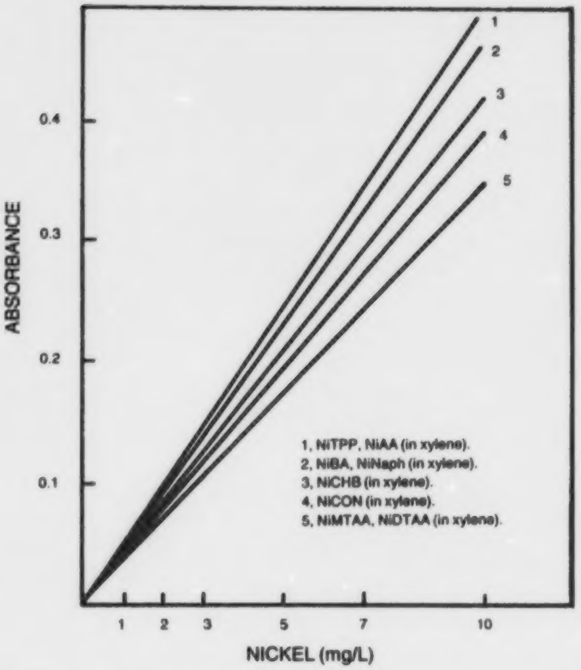


Figure 14.4: Calibration Curves for Nickel Obtained in a Nitrous Oxide-Acetylene Flame with Reference Solutions Prepared from Different Organometallic Compounds

Operating Conditions

Analytical Line	232nm
Spectral Bandwidth	0.2nm
Lamp Current	8mA
Solution Aspiration Rate	2mL/min
Observation Height	0mm (just above burner)
Nitrous Oxide Flowrate	5.0L/min
Acetylene Flowrate	4.4L/min

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iodine, bromine or chlorine in concentrations up to 400 μg/mL had no effect on the absorption signals of nickel and vanadium in xylene for either standard compounds or petroleum samples dissolved in organic solvents.[40]

Flameless Atomic Absorption

In flameless atomic absorption, a test sample is diluted with a solvent and an aliquot pipetted into a graphite boat. The sample is then pyrolyzed (ashed) and atomized without use of a flame. Abreu and Buenefama determined that the maximum ashing temperature during the analysis for some porphyrinic vanadium compounds was as low as 300°C and for nickel (II) – etioporphyrin (III) as low as 400°C.

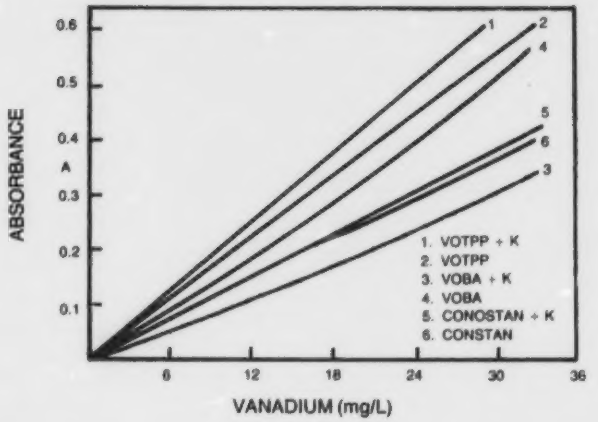

Figure 14.5: Calibration Curves for Vanadium in a Nitrous Oxide Acetylene Flame with Reference Solutions Prepared from Different Organometallic Compounds.

VOTPP: Vanadyl tetraphenylporphyrin
VOBA: bis-(1-phenyl-1,3-butandiono) oxovanadium (IV)

Operating Conditions

Analytical Line	318.4m
Spectral Bandwidth	0.33nm
Lamp Current	6mA
Solution Aspiration Rate	2.0mL/min
Observation Height	2mm above burner top
Nitrous Oxide Flowrate	5.8L/min
Acetylene Flowrate	3.4L/min

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Table 14.8: Vanadium Content in Xylene Solutions of Petroleum Samples (Reprinted with permission from Anal. Chim. Acta 1975, 78, 99- 106.)

	Vanadium (mg/L)					
	Without K			With K (2000 mg/L)		
	A	B	C	A	B	C
1	10.5	12.5	15.9	10.4	20.6	17.4
2	9.5	11.4	14.4	9.3	19.0	15.5
3	7.5	8.9	11.4	8.6	18.0	14.3
4	4.7	5.8	7.1	4.9	10.7	7.9
5	3.8	4.6	5.8	2.3	5.1	3.8

A = VOTPP reference solutions; B = VOBA reference solutions; C = Conostan reference solutions

Sample
1 a hydrogenated atmospheric residuum from Romashkino crude oil (U.S.S.R.);
2 a hydrogenated deasphaltisate from Romashkino atmospheric residuum;
3 asphaltenes from Romashkino crude oil;
4 an acetonitrile extract from Romashkino asphaltenes;
5 a vanadylporphyrin concentrate obtained by gel chromatography of sample 4.

Table 14.9: Vanadium Contents Determined by the Addition Technique in Xylene Solutions of Organometallic Standards and in Petroleum Samples (Reprinted with permission from Anal. Chim. Acta 1975, 78, 99-106.)

	Internal standard	Vanadium (mg/L) Without K Height of observation (mm) 0	2	6	With K (2000 mg/L) Height of observation (mm) 0	2	6
VOBA (6 μg/ml)	VOTPP	3.4	4.6	4.0	2.3	2.1	2.2
VOTPP (6 μg/ml)	VOBA	7.6	6.7	8.0	19.0	17.4	20.2
1	VOBA	9.5	9.4	10.1	11.8	11.4	10.3
1	VOTPP	10.8	9.8	9.9	11.2	10.6	11.9
3	VOBA	2.5	2.8	2.3	4.6	2.8	2.2
3	VOTPP	2.1	2.8	2.2	3.2	2.4	2.6

[a] Vanadium content determined after mineralization: sample 1-10.8 mg/L sample 3-1.9 mg/L.

Table 14.10: Comparison of Neutron Activation Analysis of Nickel in Heavy Crudes with Standard Curve Method and Standard Addition Method Using Carbon Rod Atomic Absorption Spectroscopy (Reprinted with permission from Appl. Spec. 1977, 31, 207-210.)

	Nickel (mg/kg) Neutron activation analysis	Standard curve method	Standard addition method
Boscan	115.7	113.9	115.6
Morichal	78.05	71.0	67.4
Cogollar	90.61	87.8	84.9

Table 14.11: Comparison of Measured Vanadium and Nickel Concentrations in Mineral Oils Obtained by Direct Dilution and Ashing Prior to Graphite Furnace Atomic Absortion (Reprinted with permission from Anal. Chim. Acta 1977, 56, 473-476.)

	Graphite furnace, dilution Vanadium (mg/kg)	Nickel (mg/kg)	Graphite furnace, ashing-dissolution Vanadium (mg/kg)	Nickel (mg/kg)
Venezuela	225	30.5	229	28.5
Middle East	22.1	8.7	22.7	7.7
Nigeria	<0.2	5.6	<0.2	4.9
Unknown 1	37.9	11.9	37.2	12.4
Unknown 2	27.2	9.8	26.4	7.8

Labrecque, Galobardes and Cohen correlated dilution-flameless AA results with neutron activation analyses in Table 14.10 for Venezuelan heavy crudes.[23] Omang's data in Table 14.11 indicate that flameless AA of a diluted crude and the same sample after wet ashing and dissolution provides equivalent results.[33] However, most of the evidence suggests that the matrix effect found in a dilution-flame AA determination also exists in dilution-flameless AA determinations. Even with careful ashing to prevent loss of metals prior to pyrolysis, Abreu and Buenefama's calibration curves for various standards differed considerably, resulting in a variety of estimates for nickel and vanadium in a crude (Tables 14.12 and 14.13). Referee analysis by neutron activation or X-ray fluorescence and dry ashing-flame AA proved that porphyrinic nickel and vanadium standards were the most suitable match for the samples examined in this study.

Grizzle and co-workers did not analyze a standard reference material as they did for direct dilution-flame AA but instead relied on a comparison with a wet ash-flame AA analysis to establish the accuracy of the flameless method. The comparisons in Table 14.14 show that good agreement was obtained.

May and Presley concluded, by comparison with neutron activation analysis, that flameless atomic absorption was too inaccurate to fingerprint residues of crude oil found on beaches. Their data, which are plotted in Figures 14.8 and 14.9, were collected without any effort to matrix-match samples and standards for the flameless AA measurements. Ashing was carried out at 1100°C which was far in excess of the permissible ashing temperature for some compounds as identified by Abreu and Buenefama. Their data do show that under fixed experimental conditions, the discrepancy between flameless AA and neutron activation can vary from zero to over 100%.

In their study of dilution-flame AA, Sebor and Lang found that the addition of approximately 20 mg/kg iodine did not suppress the matrix effects of various nickel and vanadium compounds. However, for flameless AA, Sasaki and co-workers reported that addition of iodine did

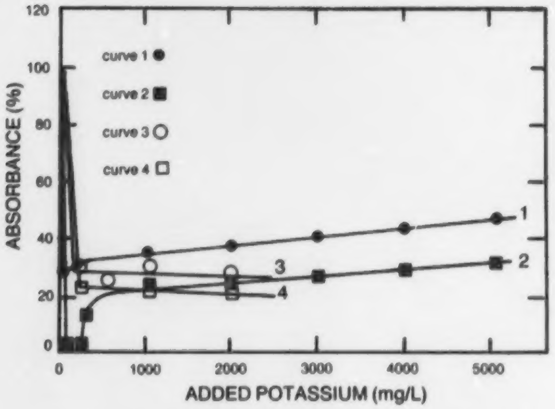

Figure 14.6: **Effect of Potassium on the Absorption Signal of 100 mg/mL Vanadium Present as VOBA.**

1. Potassium cyclohexanebutyrate (measured immediately after sample preparation). 2. Potassium cyclohexanebutyrate (measured 24 h after sample preparation). 3. Potassium Conostan standard (measured immediately after sample preparation). 4. Potassium Conostan standard (measured 24 h after sample preparation). The *y*-axis is expressed in terms of percent of absorbance when no potassium is added. (Reprinted with permission from Anal. Chim. Acta. 1977, 88, 313-318.)

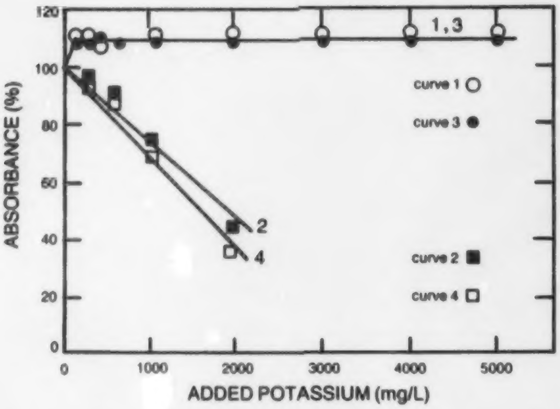

Figure 14.7: **Effect of Potassium on the Absorption Signal of Vanadium in Deasphalted Vacuum Residues**

1. Arlan crude oil, potassium cyclohexanebutyrate added. 2. Arlan crude oil, potassium Conostan standard added. 3. Romashkino crude oil, potassium cyclohexanebutyrate added. 4. Romashkino crude oil, potassium Conostan standard added. All were measured immediately after sample preparation. The *y*-axis is expressed in terms of percent of absorbance when no potassium is added. (Reprinted with permission from Anal. Chim. Acta. 1977, 88, 313-318.)

suppress the effect on the absorption signal of co-existing sodium, nickel and vanadium in a gas oil (Figure 14.10). Because these three elements should not spectrally interfere with one another, Sasaki's work suggests that the coexisting ions must somehow control the degree of formation and breakdown of stable metal complexes. The addition of iodine probably converts each metal to a single species which does not interfere with other metal species. Sasaki found that his flameless method compared well with the Japan Petroleum Institute Standard colorimetric methods in terms of both precision and accuracy (Tables 14.15 and 14.16).

Table 14.12: **Comparison of Measured Vanadium Concentration in Heavy Crude Oils Using Various Standards and Methods** (Reprinted with permission from International Symposium on the Characterization of Heavy Crudes and Petroleum Residues, Editions Technip, 1984, 179-184.)

Vanadium (mg/kg)

	Direct electrothermal determination				**Dry ashing-flame AA**	**Neutron activation analysis**
	ZVP	**JVP**	**V-CON**	**VOBA**		
Zuata	421.29 ± 11.31	407.78 ± 6.84	617.70 ± 21.66	576.27 ± 10.30	426.36 ± 11.30	425.85 ± 10.38
Merey P.	448.55 ± 27.63	435.16 ± 16.51	658.11 ± 4.63	562.14 ± 20.40	432.11 ± 11.07	434.93 ± 13.22
Hamaca	382.34 ± 4.81	356.12 ± 21.13	548.56 ± 10.70	496.80 ± 5.90	—	363.56 ± 15.80
Jobo	255.08 ± 11.56	257.28 ± 11.29	414.39 ± 12.22	445.59 ± 7.71	—	278.06 ± 13.70
Cerro Negro	481.60 ± 6.21	490.40 ± 29.18	746.74 ± 8.20	597.87 ± 12.22	460.04 ± 17.65	489.36 ± 20.11
Merey Ref.	238.63 ± 16.85	229.38 ± 4.65	397.22 ± 4.59	378.70 ± 2.43	—	250.61 ± 6.43

ZVP	Zuata Vanadyl Porphyrin
JVP	Jobo Vanadyl Porphyrin
V-CON	Vanadium Conostan Organometallic Standard
VOBA	bis(1-phenyl-1,3-butanediono)oxovanadium (IV)

Table 14.13: Comparison of Measured Nickel Concentration in Heavy Oils Using Various Standards and Methods (Reprinted with permission from International Symposium on the Characterization of Heavy Crudes and Petroleum Residues, Editions Technip, 1984, 179-184.)

	Nickel (mg/kg)			
	Direct electrothermal determination			
	Ni-CON	Ni-ETP	Dry-ashing flame AA	XRF
Zuata	135.90 ± 2.67	82.35 ± 2.20	94.35 ± 2.27	88.87 ± 1.37
Jobo	133.87 ± 5.18	82.51 ± 1.19	—	81.15 ± 1.64
Cerro Negro	152.00 ± 3.75	93.87 ± 2.55	108.59 ± 5.42	99.90 ± 1.43

Ni-CON Nickel Conostan Organometallic Standard
Ni-ETP Ni (II) Etioporphyrin (III)

Table 14.14: Vanadium and Nickel Concentrations as Determined by Flame-Analyzed Wet Ashing, Flameless Dilution, and Direct Flameless Methods[15]

	Nickel (mg/kg)			Vanadium (mg/kg)		
	Flame AA-wet ashing	Flameless AA		Flame AA-wet ashing	Flameless AA	
		Dilution	Direct		Dilution	Direct
Village Mills, East Texas	0.6	0.26 ± 0.02	0.28 ± 0.01	0.1	ND	0.67 ± 0.23
Kismet, Northwest Kansas	6.6	8.79 ± 0.98	8.33 ± 0.20	17.2	23.02 ± 1.47	—
Earlsboro, Oklahoma	1.4	1.16 ± 0.05	1.14 ± 0.05	2.4	2.39 ± 0.31	2.23 ± 0.27
Shoal, Louisiana	0.9	0.92 ± 0.05	0.62 ± 0.01	0.4	ND	0.73 ± 0.32
Sooner Trand, Oklahoma	0.4	0.57 ± 0.02	0.50 ± 0.08	1.1	2.30 ± 0.19	1.37 ± 0.16
Unknown	33.7	36.0 ± 1.6	—	ND	—	—
Unknown	58.2	62.4 ± 1.9	—	442.2	507.3 ± 20.3	—
Unknown	8.8	7.73 ± 0.80	8.00 ± 0.40	28.2	21.1 ± 20.3	—

ND: Not detectable under the conditions employed

Table 14.15: Comparison of Measured Nickel and Vanadium Levels in Oils Using a Graphite Furnace Atomic Absorption Method Requiring Addition of Iodine and the JPI Colorimetric Method[37]

		Metal content (mg/kg)	
		Flameless method	JPI method
Atmospheric distillation residue	Ni	36.1	37
	V	103.7	104
Arabian light crude	Ni	2.1	3.0
	V	6.7	7.5

Table 14.16: Comparison of Repeatability of Graphite Furnace Atomic Absorption Method Requiring Addition of Iodine and the JPI Colorimetric Method[37]

		Flameless method	JPI method
	Concentration (mg/kg)	Repeatability (mg/kg)	Repeatability (mg/kg)
Nickel	1-10	0.2	1
	31-40	4.0	3
Vanadium	15	1.2	1.4-1.6
	70	9.4	6.3

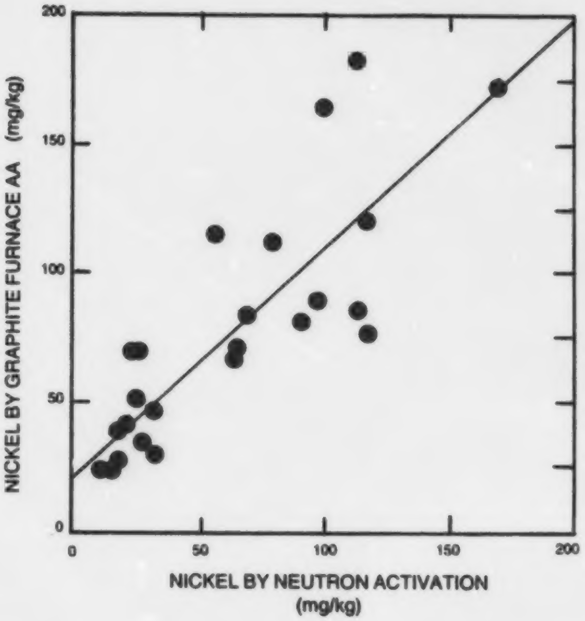

Figure 14.8: **Comparison of Graphite Furnace Atomic Absorption and Neutron Activation Data for Nickel in Beach Asphalt**[28] The best-fitting straight line is $y = 0.93x + 16.54$. The standard deviations of the slope and intercept are 0.13 and 10.44 respectively.

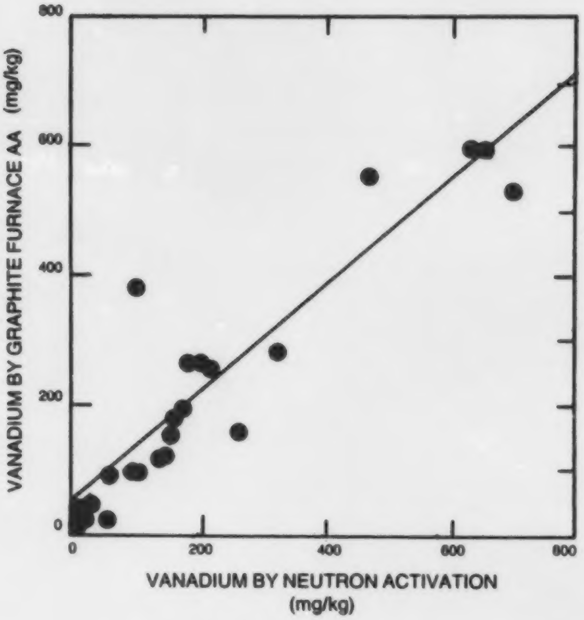

Figure 14.9: **Comparison of Graphite Furnace Atomic Absorption and Neutron Activation Data for Vanadium in Beach Asphalt**[27] The best-fitting straight line is $y = 0.85x + 31.41$. The standard deviations of the slope and intercept are 0.07 and 20.02 respectively.

Other Aspects of Sample Preparation

Unlike elements such as iron, sodium and potassium, which are present in high levels in oil sand solids and which may be measured as organo-metallics if suitable solids-removal procedures are not employed prior to measurement, nickel and vanadium determinations in Athabasca oil sand are not affected by low levels of solids. Jacobs and Filby measured, by neutron activation, levels of thirty metals in a test sample of Athabasca bitumen containing fines. The fines were subsequently removed from the bitumen and the metals content of the bitumen on a solids-free basis was estimated.[21] The results for nickel and vanadium as well as iron, sodium and potassium are given in Table 14.17.

Table 14.17: **Trace Element Concentration in Athabasca Samples** (Reprinted with permission from Anal. Chem. 1983, 55, 74-77. Copyright 1983, American Chemical Society.)

	Metal content (mg/kg)				
	Ni	V	Fe	Na	K
Sample 1					
Bitumen	68.1 ± 8.0	144 ± 19	1030 ± 70	149 ± 10	594 ± 45
Fines	52.0 ± 7.7	142 ± 16	26600 ± 800	2750 ± 7	16800;30
Mineral-free bitumen	66.3 ± 8.0	139 ± 19	<200	52 ± 12	0
Sample 2					
Bitumen	71.0 ± 16	170 ± 5	242 ± 17	21.2 ± 3.0	44.3 ± 2.9
Fines	69.0 ± 17	194 ± 24	27500 ± 4100	2110 ± 13	17.200 ± 64
Mineral-free bitumen	70.3 ± 6	170 ± 5	171 ± 21	15.8 ± 3.0	0

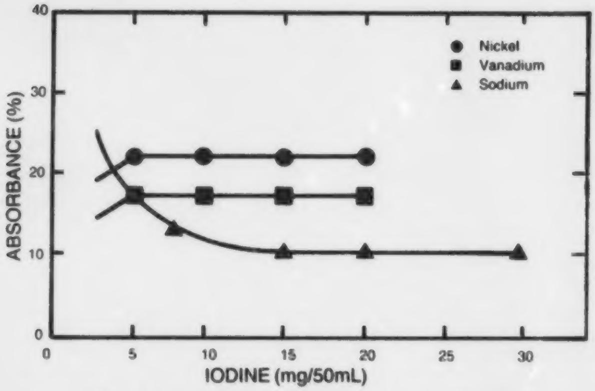

Figure 14.10: **Effect of Iodine on Graphite Furnace Atomic Absorption Signals of Coexisting Nickel, Vanadium and Sodium in Gas Oil[37]**

Reichert and co-workers reported an unusual case in which the measured vanadium and nickel levels of upgrading residues were lowered when the sample was dissolved in xylene, filtered, and aspirated directly.[35] Their data, given in Table 14.18, can be explained by considering that the residue may have contained a large proportion of organic, but insoluble, metal-bearing material. Calibration errors as described earlier may also have contributed to the discrepancy.

Results of Cooperative Studies

In both the ACOSA and Phillips cooperative studies, such a variety of ashing or direct dilution methods in combination with flame AA, flameless AA and ICP methods were used that the precision of specific methods could not be calculated. Both studies indicated that there are serious difficulties in obtaining reliable estimates of nickel and vanadium in heavy crudes. Overall precision statements from the studies are given in Table 14.19. Reproducibility did not improve when methods involving a preliminary ashing were considered alone, probably because a variety of ashing techniques was used.

Table 14.18: **Vanadium and Nickel Content of Upgrading Residues Obtained Using Atomic Absorption with Different Sample Preparation Methods[35]**

		Metal content (mg/kg)	
Sample	Metal	Ashing-acid dissolution	Dissolution in xylene-filtration
1	V	179	10
	Ni	147	60
2	V	1850	13
	Ni	690	17
3	V	18	12
	Ni	16	20
4	V	33	29
	Ni	34	32

In other studies in which the ashing as well as the measurement techniques were rigidly defined, precision was much better. The results of a study sponsored by the Japan Petroleum Institute in which thirty-four laboratories carried out duplicate analyses of three crude samples are summarized in Table 14.20.

A study by the German Society for Petroleum Sciences and Coal Chemistry's study, summarized in Table 14.21, also defined sample preparation and test conditions. Here, dry ashing was carried out at 550°C and nickel and vanadium standards from Merck AG were used for calibration in all of the laboratories.

Other Methods

Neutron activation, X-ray fluorescence, and atomic emission using a spectrograph have been used for the measurement of trace metals in crudes. The former is not widely used because of the scarcity of neutron generators for routine work. X-ray fluorescence requires matrix matching of standards with samples in terms of both C/H ratio and sulfur content. Yousif and Al-Shar-

Table 14.19: **Precision of Trace Metal Determinations from ACOSA and Phillips Cooperative Studies**

	Nickel (mg/kg)		Vanadium (mg/kg)	
	Repeatability	Reproducibility	Repeatability	Reproducibility
ACOSA[a]	14	20	20	85
Phillips[b]				
California	19	28	22	61
Maya			18	124

[a] Eighteen laboratories conducted duplicate analyses of an Athabasca bitumen containing approximately 75 mg/kg Ni and 220 mg/kg V, and a Lloydminster heavy oil containing approximately 55 mg/kg Ni and 150 mg/kg V. Data from one laboratory reporting 17 mg/kg Ni in the Athabasca sample and from a second laboratory reporting 263 mg/kg V in the Lloydminster sample were disregarded.

[b] Fifteen laboratories conducted duplicate analyses of a California heavy oil blend with approximately 75 mg/kg Ni and 190 mg/kg V, and a Maya crude with approximately 55 mg/kg Ni and 240 mg/kg V.[34]

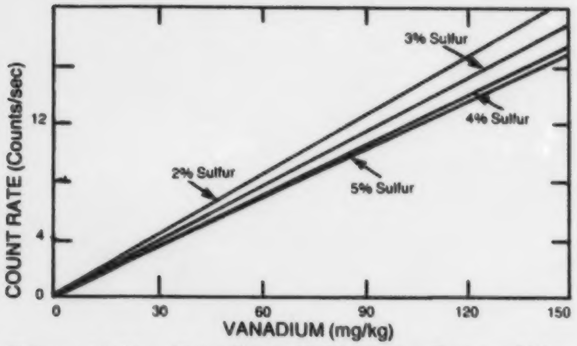

Figure 14.11: **Vanadium Calibration Curves Using XRF at Different Concentrations of Sulfur in Crude Oils** (Reprinted with permission from Int. J. Appl. Rad. Isot. 1977, 28, 759-763. Copyright 1977, Pergamon Press Ltd.)

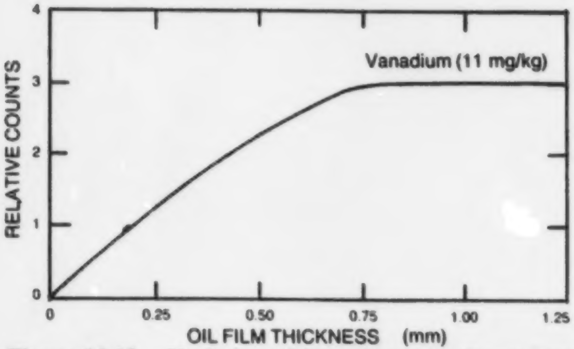

Figure 14.12: **Variation of Vanadium Kα Count Rate with Oil Film Thickness** (Reprinted with permission from Int. J. Appl. Rad. Isot. 1977, 28, 759-763. Copyright 1977, Pergamon Press Ltd.)

Table 14.20: Precision of Trace Metal Determinations from a Japan Petroleum Institute Study[32]

	Nickel (mg/kg)			Vanadium (mg/kg)		
	Mean	**Repeatability**	**Reproducibility**	**Mean**	**Repeatability**	**Reproducibility**
Sample 1						
Method 1	2.26	0.29	0.47	8.79	0.54	1.91
Method 2	2.69	0.33	0.58	8.89	0.87	2.93
Method 3	2.58	0.24	0.60	8.70	0.96	2.32
Sample 2						
Method 1	16.00	1.06	3.06	39.70	1.93	4.89
Method 2	16.78	1.67	3.21	42.23	3.97	16.62
Method 3	16.38	0.74	2.48	41.30	5.52	17.27
Sample 3						
Method 1	24.61	1.37	2.65	73.15	1.82	8.88
Method 2	24.78	1.66	3.56	70.35	4.17	24.71
Method 3	23.91	1.22	3.76	69.63	8.49	21.12

Methods

1) Wet ashing with H_2SO_4 at 525° C followed by JPI-5S-10-79 colorimetric method for nickel and JPI-5S-11-74T colorimetric method for vanadium.

2) Wet ashing with H_2SO_4 at 525°C followed by flame AA

3) Dry ashing with H_2SO_4 at 525°C followed by flame AA

Table 14.21: Comparison of Data from DMGK Round Robin Studies[12]

	Nickel (mg/kg)			Vanadium (mg/kg)		
Sample	**Lab 1 AA**	**Lab 2 AA**	**Lab 3 XRF**	**Lab 1 AA**	**Lab 2 AA**	**Lab 3 XRF**
BOSCAN B 80						
Vacuum residue	90	99	99	342	276	300
Asphalts	399	462	484	1362	1029	1431
Colloids	372	413	452	1267	952	1319
Dispersants	28	45	37	106	92	113
SAFANIJA B 45						
Vaccum residue	40	47	50	150	116	160
Asphalts	128	137	162	474	301	490
Colloids	103	109	129	360	245	454
Dispersants	5.2	7	7	26	26	29

istani gave examples of vanadium calibration curves at different concentrations of sulfur in crude oils (Figure 14.11). They also determined that in their system a minimum oil film thickness of 0.75 mm was required (Figure 14.12).

Gamble and Jones developed a wet ash spectrographic method for determining the level of trace metals in petroleums.[13] UOP Method 389-71 describes the determination of trace metals in oils by obtaining a spark spectrum of a solution of metals using a rotating-disk electrode technique. The densities of the metal lines are measured by microphotometer; concentrations are determined from standard calibration curves. The repeatability for metals in the concentration range of 1 to 200 mg/kg is approximately 25% relative. UOP now uses atomic absorption rather than this method in their routine work.

SUMMARY

Because some metal porphyrins volatilize at temperatures as low as 300°C, a wet ashing method for destruction of the sample matrix and conversion of metals to a relatively involatile form is preferred over dry ashing. If the nickel and vanadium are converted to sulfates, an ashing temperature of 525°C can be used without loss of the metals. Cooperative studies in which the ashing of samples and dissolution of the metals were defined, and a single calibrating standard was used, yielded much better precision than cooperative studies in which each laboratory has followed its own procedure.

Dilution of the sample followed by flame or flameless atomic absorption is an unreliable method for determining the level of nickel and vanadium in bitumens and heavy oils. The slope of the calibration curve is controlled by the nature of the metal compound. Internal standard addition does not reduce the error.

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Chapter 15: DISTILLATION

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DISTILLATION

TRUE BOILING POINT (TBP) DISTILLATION

DEFINITION

A true boiling point (TBP) distillation is one in which the test sample is physically distilled to produce fractions of the desired cutpoints.

SIGNIFICANCE

A bitumen or crude oil sample is distilled to determine the quantity of hydrocarbon in different boiling point ranges, and to generate specific fractions for further analyses. ASTM standards describe distillation methods for pitches (D2569), cut-back asphalts (D402), and petroleum products (D86). Most of these methods specify an upper atmospheric equivalent temperature (AET) limit of 360°C and therefore are too limited to be of value in the analysis of bitumen.

Four distillation procedures are commonly used by laboratories, either singly or in combination, to determine the distillation curve of, or produce fractions from, bitumens and heavy oils. They are:

- ASTM D2892: Distillation of Crude Petroleum (15-Theoretical-Plate Column)
- ASTM D1160: Distillation of Petroleum Products at Reduced Pressures
- spinning band distillation
- distillation using a flash still.

METHODS

1. ASTM D2892: Distillation of Crude Petroleum

1.1 Application

This method describes the procedure for distilling crude petroleum up to 400°C AET. Crude oil samples containing light components must be debutanized in a preliminary step.

1.2 Summary of the Method

A weighed sample of 1 to 10 litres is distilled in a fractionating column having an efficiency at total reflux of 14 to 18 theoretical plates. A reflux ratio of 5:1 is maintained throughout except at the minimum pressure of 2 mm Hg where a ratio of 2:1 can be used. The mass and density of each cut are used to prepare distillation curves either by mass or volume. This method is commonly called the "15/5" method.

1.3 Precision

Cut Point, (°C AET)	Reproducibility[a] (LV or Weight %)
to 204	0.7
205 to 300	0.9
301 to 400	0.9

[a] From analysis by eight laboratories of a medium gravity (Mid-Continent, U.S.) crude with a relative density (15°C/15°C) of 0.835.

2. ASTM D1160: Distillation of Petroleum Products at Reduced Pressures

2.1 Application

This method covers the determination of boiling temperature ranges of petroleum products to a maximum liquid temperature of 400°C at pressures as low as 1 mm Hg.

2.2 Summary of the Method

A 200-mL sample is weighed to the nearest 0.1 g in a distillation flask. The distillation assembly is evacuated to the desired pressure and heat is applied to the flask as rapidly as possible using a 750-W heater. When refluxing liquid appears, the rate of heating is adjusted so that the distillate is recovered at 4 to 8 mL/min until the distillation is complete.

Cracking of the bitumen may occur before the liquid temperature reaches 400°C. An increase in distillation rate accompanied by a drop in head temperature, loss of vacuum in the system which is restored when heat to the still is reduced, and production of vapor clouds in the system are all evidence of cracking.[7]

2.3 Precision

	Repeatability (C°)	Reproducibility (C°)
Pressure		
1 mm Hg, absolute:		
5% recovered and greater	5.5	16.6
10% recovered and greater		11.1
10 mm Hg, absolute:		
5% recovered and greater	4.4	11.1
10% recovered and greater		8.3
50 mm Hg, and higher:		
5% recovered and greater	5.5	16.6
10% recovered and greater		11.1

3. Syncrude Analytical Method 5.2: Spinning Band Distillation of Liquid Hydrocarbons and Bitumen

3.1 Application

Fractions of bitumen and liquid hydrocarbon samples with an initial boiling point above room temperature at atmospheric pressure can be prepared using this method. When fractionating bitumen, the pot temperature cannot exceed 360°C.

3.2 Summary of the Method

Samples are distilled under atmospheric and reduced pressures in a still equipped with a spinning band column. Vapor temperatures are converted to AET's using equations given in the method. AET can be plotted as a function of volume or weight percent distilled to yield a distillation curve.

3.3 Precision

Precision data reflecting the repeatability of weight percent distillate fraction determinations for a typical Athabasca bitumen are indicated below. Results are based on four or more complete distillations performed by a single operator on charges obtained from homogeneous stock.

	Mean (%)	Repeatability (%)	Repeatability (% Relative)
LGO (195-343°C)	12.50	0.45	3.69
HGO (343-524°C)	27.24	1.50	5.51
Residue (524°C)	58.23	0.82	1.41
Recovery (%)	99.26	0.28	0.28

The three distillation cuts listed above are defined by the temperature ranges given. In practice, distillation of bitumen can rarely be carried beyond an AET of 450°C. Therefore, the true cutpoints for HGO and residue should always be given. The table above indicates that approximately 0.7% of the sample remains as hold-up in the system.

4. Collection of Fractions using a Flash Still (Short Path Distillation)[2,9]

4.1 Application

Short path distillation produces a single distillate and a single residue fraction defined by the operating temperature and pressure of the still. This procedure is used to generate high boiling point fractions with endpoints up to 700°C for further analysis. Since only one cut temperature is used in each run, generation of a distillation curve using this equipment would be time consuming.

4.2 Summary of the Method

The material to be fractionated is introduced at a constant rate onto the hot inner wall of the evaporator under high vacuum. Rotating teflon rollers ensure that the film on the wall is kept thin. The feedstock is progressively distilled at the fixed conditions of temperature and pressure. The distillate vapors condense on a

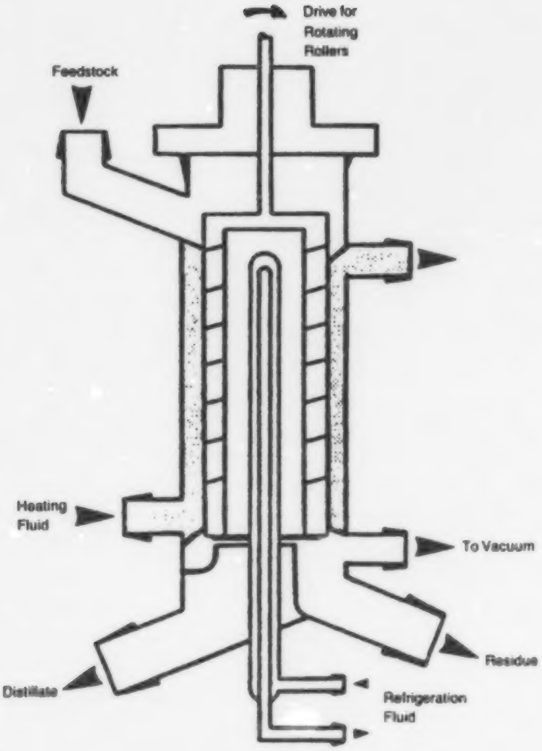

Figure 15.1: Schematic of the Distact Short Path Distillation Apparatus

concentric cold surface (60°C) placed inside and a short distance from the hot wall. The condensate then drains by gravity to the base of the "cold finger" where it is collected. The residue drains down the hot wall and is collected through a separate port. Figure 15.1 is a diagram of the apparatus.

4.3 Precision

Not available. The degree of overlap between the distillate and the residue is a function of the operating conditions of the distillation.

5. UOP 109 - 84: Vacuum Distillation of Topped Crude Oils and Similar Petroleum Products

5.1 Application

This method describes the determination of the amount of distillate fractions and residue from topped crude oils and similar petroleum products with initial boiling points above 200°C. A maximum AET of 560°C can be achieved.

5.2 Summary of the Method

Test samples ranging from 0.5 to 4 litres are distilled under a vacuum of 0.2 to 0.3 mm Hg by applying heat with a gas burner. Unlike ASTM D1160, provisions are made for collecting numerous fractions during the distillation for further analyses and for preparing a distillation curve. UOP intends to replace the equipment described in this method with ASTM equipment when the ASTM potstill method is approved.

5.3 Precision

Not established.

6. Distillation of Heavy Oils and Crudes (By Vacuum Potstill Method)

6.1 Application

This method describes the distillation of heavy crudes, petroleum distillates and residue having initial boiling points above 150°C. It is currently being ballotted for inclusion in the 1987 ASTM gray pages.

6.2 Summary of the Method

A weighed sample of 0.5 to 4 litres in volume is distilled under vacuum to a maximum temperature of 565°C AET. Cuts may be taken at any point for further analysis and for preparation of a distillation curve.

6.3 Precision

Not established.

GAS CHROMATOGRAPHIC SIMULATED DISTILLATION (GCD)

DEFINITION

A gas chromatographic distillation (GCD) employs gas-liquid chromatography to separate compounds by boiling point and produce a distillation curve.

SIGNIFICANCE

In comparison to an actual distillation, GCD requires a very small sample (several microlitres) to give a full boiling range distribution curve for prediction of distillate yield and residue. GCD takes two hours whereas a full distillation may take two days.

Simulated distillation for distillate fractions, ASTM D2887, is well established and used by many laboratories. This method, however, is designed for samples with a final boiling point below 538°C, and is not suitable for the analysis of bitumens and heavy oils. ASTM Committee D2 has proposed a test method, proposal P167, that can handle such samples. It has not been formally ratified by ASTM participants, but many laboratories have adopted it as a method for analyzing heavy crudes. Syncrude Analytical Method 5.3 is an adaptation of the method.

7. ASTM D2 Proposal P167: Boiling Range Distribution of Crude Petroleum by Gas Chromatography

7.1 Application

This method covers the determination of the boiling range distribution of crude petroleum samples which can be dissolved in a solvent to permit sampling with a micro-syringe. The test sample must contain less than 0.2% water.

7.2 Summary of the Method

The test sample is diluted with carbon disulfide and the solution is injected into a gas chromatographic column containing 3 to 10% of a silicone gum rubber or equivalent liquid phase on a diatomaceous earth support. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve obtained under the same conditions by running a mixture of n-paraffins from C_4 to C_{44} of known boiling points up to a temperature of 538°C (1000°F).

The amount of sample boiling above 538°C is estimated in a second chromatographic run by injecting the sample and an internal standard mixture (usually C_{14}, C_{16}, C_{18} and C_{20}) and separating the fractions under conditions identical to those for the sample alone. The boiling range distributions are then calculated from the areas of sections of the chromatograms.

7.3 Precision

Not established.

8. Syncrude Analytical Method 5.3: Gas Chromatographic Simulated Distillation of Hydrocarbon Samples Containing Nonvolatile Residue

8.1 Application

This method is intended for the simulated distillation of bitumens and other samples that have a final boiling point above 525°C.

8.2 Summary of the Method

A calibration standard comprising a mixture of C_5 to C_{44} normal paraffins is analyzed on a gas chromatograph to relate retention time to actual boiling point. A response factor is determined by injecting a mixture of 1% naphthalene and 99% heavy gas oil which can be prepared by spinning band distillation or by commercial production.

To analyze an unknown sample, two chromatographic runs are required. In the first, the unknown sample is diluted with CS_2 before the run. The second run is conducted on a mixture of 2% naphthalene and 98% sample diluted with CS_2. Calculations are then conducted to first determine the fraction of the sample which boils below 525°C, and then the distillation curve for that fraction.

8.3 Precision

Not established.

DISCUSSION

Removal of Water from Test Samples of Crude

The presence of more then 0.5% water in test samples of crude can cause several problems during TBP distillations. Water has a high heat of vaporization, necessitating the addition of extra heat to the distillation flask. Water is easily superheated and therefore excessive "bumping" can occur, leading to breakage of glass distillation systems. Steam formed during distillation can act as a carrier gas and high boiling point components may end up in the distillate.

Centrifugation can be used to remove water (and sediment) if the sample is not a tight emulsion. Gouw described other methods that are used to remove water.[5] They include:

- heating in a pressure vessel to control loss of light ends
- addition of calcium chloride as recommended in ASTM D1160
- addition of an azeotroping agent such as isopropanol or n-butanol

Table 15.1: Short Path Distillation Yields from an Athabasca Bitumen 343+°C Residue (Reprinted with permission from AOSTRA J. Research 1986, 2, 191-196.)

Pressure: 10^{-3} mm Hg
Feed rate: 0.18 L/h
Roller speed: 250 rpm

Assay temperature (°C)	Cutpoint (°C)	Distillate yield by short path distillation (wt. %)	Distillate yield by GCD (wt. %)
150	475	26.5	27
175	500	31.3	31
210	540	39.6	39
250	580	47.4	47
290	620	54.9	54
325	660	60.4	—
D1160 limit	524[b]	37.9	

[a] Cut points were estimated from GC distillation data for the feed.

[b] The D1160 distillation produced an "observed" distillation cut point of 524°C.

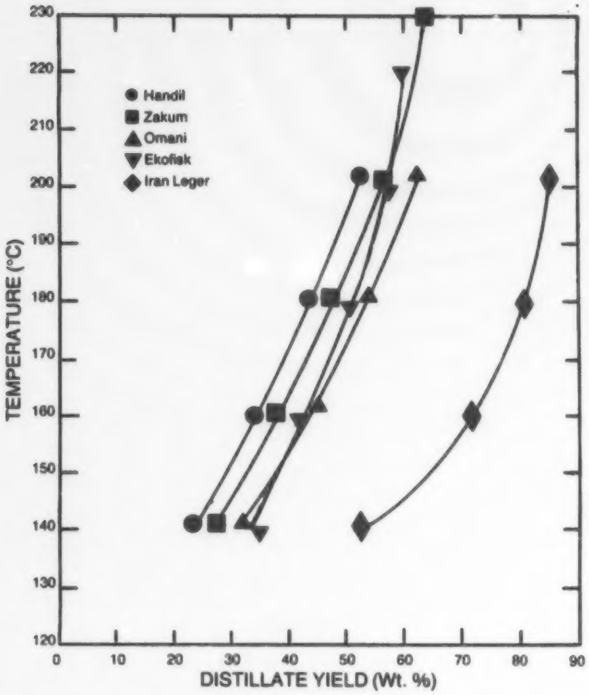

Figure 15.2: Distillate Yield for Various 375 + °C Residues vs. Distillation Temperature in a Short Path Distillation Apparatus (Reprinted with permission from Analusis 1982, 10, 57-70.)

Feed rate: 0.20 L/h
Vacuum: <0.001 mb
Roller speed: 400 rpm

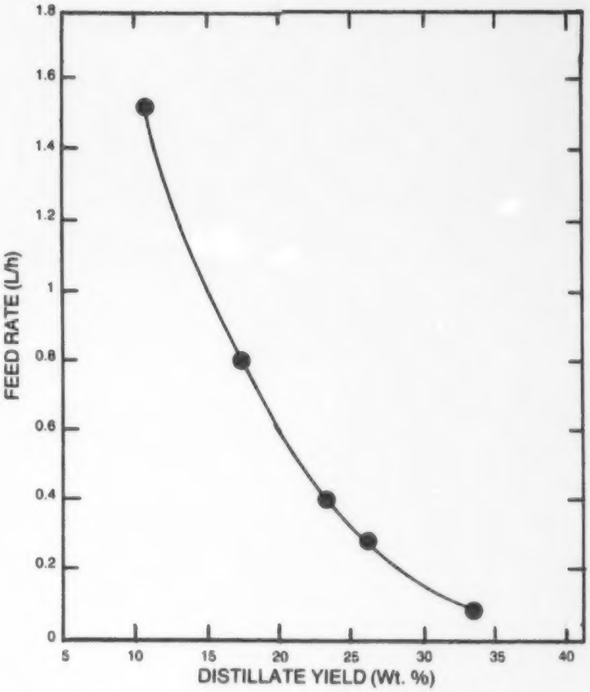

Figure 15.3: Distillate Yield for a 350 + °C Residue of Iraqi Crude vs. Feed Rate in a Short Path Distillation Apparatus (Reprinted with permission from Analusis 1982, 10, 57-70.)

Distillation temperature: 150°C
Vacuum: <0.001 mb
Roller speed: 400 rpm

- removal of water in a preliminary low-efficiency or flash distillation followed by reblending of the hydrocarbon which co-distills with the water into the sample.
- separation of the water from the hydrocarbon distillate by freezing.

Short Path Distillation

Short path distillation permits collection of deeper cut distillate and residue fractions than conventional vacuum distillation methods. AET endpoints of up to 660°C can be attained without thermal cracking of the material. The distillation, however, is conducted under non-equilibrium conditions so the cutpoint is not as specific as in other vacuum distillation methods.

Vercier and Mouton[13] described the effect of temperature, rotation speed of the rollers, and feed rate on the percent distilled from several residues (Figures 15.2 to 15.4). Domansky[1] reported the percent distilled from an Athabasca bitumen residue (343 + °C) as a function of assay temperature with other conditions constant (Table 15.1). In Table 15.1 the percent of material distilled as estimated by GCD is also provided for each of the estimated short path distillation cutpoints.

Determining the Amount of Residue in a Heavy Crude

ASTM D2887 cannot be used to determine the distillation curve of bitumens and heavy oils because it does not provide for the determination of the proportion of 538 + °C residue in the test sample. The use of internal standards, and combinations of actual distillations and GCD which provide a distillate fraction which can then be analyzed by gas chromatography, have already gained wide acceptance in the industry. They are discussed in the section following this.

Philyaw and co-workers attempted to determine the percent residue of a crude by combining the principles of GCD with elemental analysis.[10] They injected the test sample into a port set at approximately 350°C and carried out the GCD in a routine manner up to the maximum permissible column temperature. The effluent from the

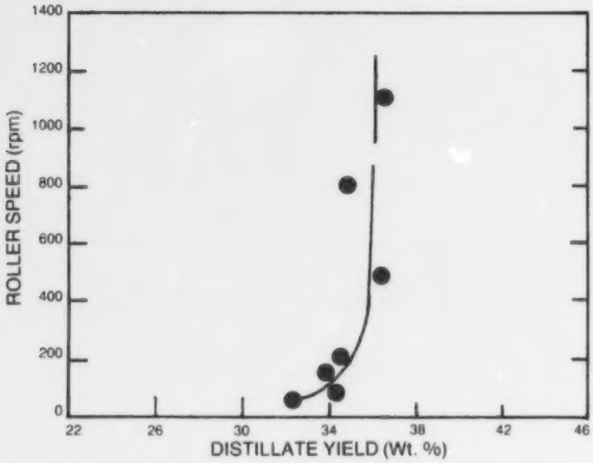

Figure 15.4: Distillate Yield for an Industrial Residue of Iraqi Crude vs. Roller Speed in a Short Path Distillation Apparatus (Reprinted with permission from Analusis 1982, 10, 57-70.)

Feed rate: 0.2 L/h
Distillation temperature: 180°C
Vacuum: <0.00/mb

column passed into a furnace containing copper oxide to convert the organic components to carbon dioxide which was measured by thermal conductivity. After the GCD was completed, the flow of carrier gas through the column was reversed to remove any material that vaporized in the injection port but did not pass completely through the column. Then the temperature of the injection port was raised to 700°C to crack and remove much of the sample which did not initially vaporize. Finally the coke was removed from the port by introducing oxygen at 700°C. The gases from these three steps were measured in the manner described.

A typical chromatogram is shown in Figure 15.5. A comparison of the percent residue in four heavy oils as determined by Philyaw's method and by actual distillation on a 30-plate Oldershaw column followed by a vacuum Engler distillation is provided in Table 15.2. Complete distillation curves by the same two methods are given for a heavy Mississippi crude in Figure 15.6.

Southern and co-workers calculated the distillation curves of coal-derived liquids by a combination of GCD of the whole sample and vacuum thermogravimetry to determine the amount of residue.[11] The same principle should be applicable to bitumen and heavy oil. Several precautions must be taken to ensure accurate and precise determinations of the residue by this method. Errors are minimized by:

- using a strong vacuum pump and controlled gas bleed with the capacity to quickly remove the sample vapor while maintaining constant vacuum.

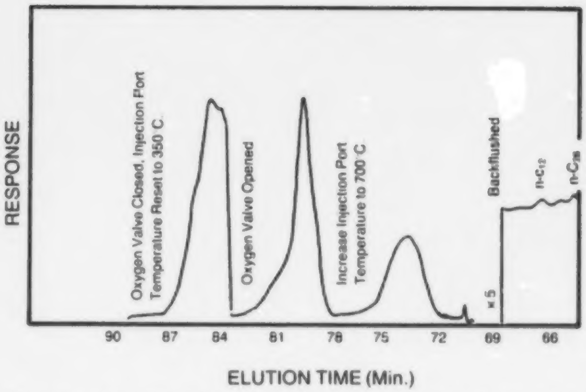

Figure 15.5: Residue Peaks Obtained by GLC Anaysis of Heidelberg- Eucutta-Yellow Creek (Mississippi) Crude Oil (Reprinted with permission from Anal. Chem. 1971, 43, 787-789. Copyright 1971, American Chemical Society.)

- locating the vacuum gauge as close to the sample container as possible.
- holding the sample mass/surface area ratio to a maximum of 30 mg/65 mm^2 to reduce splattering.
- working at vacuum pressures which are no lower than necessary to minimize error in the conversion to AET, while achieving the necessary temperature endpoint without cracking the sample.
- employing a heating rate no greater than 10°C/min so that heat transfer through the sample occurs quickly relative to the heating rate. The use of a slow heating rate also eliminates the effects of sample cooling due to the endothermic nature of volatilization and thermal lag due to the distance between the thermocouple and the sample surface.
- correcting for the change in buoyancy of the balance beam with temperature.

Table 15.2: Comparison of Residue Recovery for Heavy Crude Oils from Simulated Distillation with Elemental Analysis of the Eluent (Reprinted with permission from Anal. Chem. 1971, 43, 787-789. Copyright 1971, American Chemical Society)

		Residue (wt. %)	
	Actual distillation	**Before O_2 burn**	**O_2 burn**
Heidelberg/Eucutta/ Yellow Creek (Mississippi)	27.1	18.9	27.3
Lagomar (Venezuela)	37.9	31.8	37.6
Heavy Valley (California)	54.6	41.2	54.0
Baxterville (Mississippi)	55.7	45.1	55.3

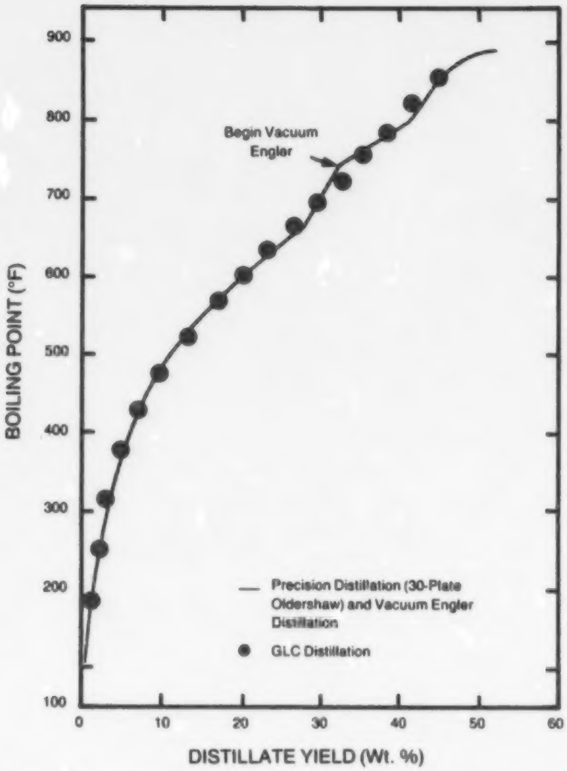

Figure 15.6: Comparative TBP Analysis of Baxterville (Mississippi) Crude by Distillation and GLC (Reprinted with permission from Anal. Chem. 1971, 43, 787-789. Copyright 1971, American Chemical Society).

Once these factors are controlled, precise (±2% relative) estimates of the residue in a sample can be obtained (Table 15.3).

Quality of TBP Distillations as Defined by GCD and Correlation of GCD with TBP Distillations

The quality of distillation, that is the degree of overlap between one cut and the next, is important in the evaluation of fractions from a crude. Typically, in a high-quality distillation, the contamination will be 2 to 4% of total crude at each cut temperature.

Flooding of the column and cracking of the feedstock are two serious problems during a TBP distillation. Flooding, which results from an excessive rate of heating, is the physical transport of liquid up the column and into the receiver. Cracking is thermal degradation of crude oil caused by high temperatures in the distillation pot, and can occur at any temperature above 250°C, depending on the crude. It is indicated by the formation of a "fog" in the distillation pot or column, a sudden drop of vapor temperature at the top of the column, or by the presence of light components in the heavy fractions as measured by GCD.

The measurement of pressure at the top of the distillation column is critical to valid distillation results because the observed vapor temperature must be corrected to the equivalent temperature (AET) at standard pressure conditions (760 mm Hg). Some laboratories that have studied vacuum distillation have shown that the minimum pressure should be 2 mm Hg or greater for reasonably accurate measurements and correction to AET. At pressures below 2 mm Hg, the pressure measurement is too inaccurate and a discontinuity can arise in the AET distillation curve from atmospheric to vacuum distillation.

Fuhr and Klein conducted spinning band and simulated distillations on an Athabasca (Suncor) coker feed bitumen.[3] The two distillation curves shown in Figure 15.7 are similar up to the endpoint of the spinning band distillation curve at 469°C. Fractions collected from the spinning band distillation were subsequently analyzed by GCD to assess the quality of the distillation. The data, given in Table 15.4 indicate some difficulty in obtaining a good naphtha fraction, but the remaining fractions were relatively clean as defined by GCD.

A large body of data is available for GCD - TBP correlations developed for conventional crude oils which have final boiling points above 538°C. McTaggart and co-workers compared the distillation data from three GCD

Table 15.3: Repeatability of Vacuum TGA Residuum Determination[a,11] (Reprinted with permission from Anal. Chem. 1984, 57, 303-308. Copyright 1984, American Chemical Society.)

	Sample A Residue AET = 538°C (wt.%)	**Sample B Residue AET = 535°C (wt.%)**
Run		
1	56.1	49.0
2	54.4	49.5
3	55.4	49.8
4	52.7	49.6
5	53.5	
6	55.9	
7	54.1	
8	54.9	
9	53.9	
$\bar{x}$	54.5	49.5
s	1.1	0.3
Repeatability	3.2	1.0

[a] Conditions: sample size, 5-8 mg; container type, flat AL pan (28 mm^2, 0.5 mm); and vacuum level, 0.3-0.9 mm Hg.

methods to 15 plate distillation data (ASTM D2892) for crudes from Kuwait, Nigeria, Iran and Qatar.[8] The methods were GCD by ASTM D2887 of flash distillates from a miniature flash still which is shown in Figure 15.8, addition of a single n-paraffin to the crude oil as an internal standard to quantify the weight of crude oil eluted from the gas chromatographic column, and the addition of four n-paraffins to the crude to quantify the weight of crude eluted from the column. In the latter method, the crude and the mixture of crude plus internal standard are analyzed separately as in the ASTM D2 proposal.

Because all the samples were paraffinic it was not necessary to calibrate the boiling point scale; the internal standards used in the internal standard methods above were sufficient to provide temperature calibration. Tables 15.5 summarizes the results of repeat distillations of the Kuwaiti crude using the three methods, and compares the results of those methods with ASTM D2892 data.

McTaggart found no flash temperature that would remove all of the 500°C material from the crudes without flashing some of the heavier fractions. When the distillate produced by flashing a Kuwait crude at 380°C under vacuum was analyzed by ASTM D2887, the resulting distillation curve gave a difference of 3% in the amount of material boiling at 500°C AET. This discrepancy, due to the incomplete distillation of the 500°C fraction from the residue, may be acceptable in some applications. Since no heavy ends are introduced onto the GC column, contamination of the system is not possible. Use of a higher flash temperature is not recommended because some 500+°C materials would also be distilled. As a footnote to McTaggart's study of the flash still, there is no reason why ASTM D2892 cannot be used to provide the distillate fraction. These should provide cleaner cut-points than flash distillation; however, the time required to produce the fractions by actual distillation compared to the flash distillation would be a drawback.

Table 15.4: Quality of Spinning Band Distillation Fractions as Determined by GCD[3]

	GCD		Wt. % of the fraction distilled by GCD at the spinning band temperature	
Spinning band cut	**IBP**	**FBP**	**IBP**	**FBP**
Naphtha 121- 195°C	90	218	4	80
Light gas oil 195 - 343°C	190	351	1	97
Heavy gas oil[a] 343 - 469°C	325	489	4	88
Residue >469°C	461	–	1	–

[a] The heavy gas oil cut point was the highest AET which could be reached on the spinning band unit without cracking.

The precision and accuracy of the single internal standard method depends on the accuracy of estimating the area of the internal standard. The amount of internal

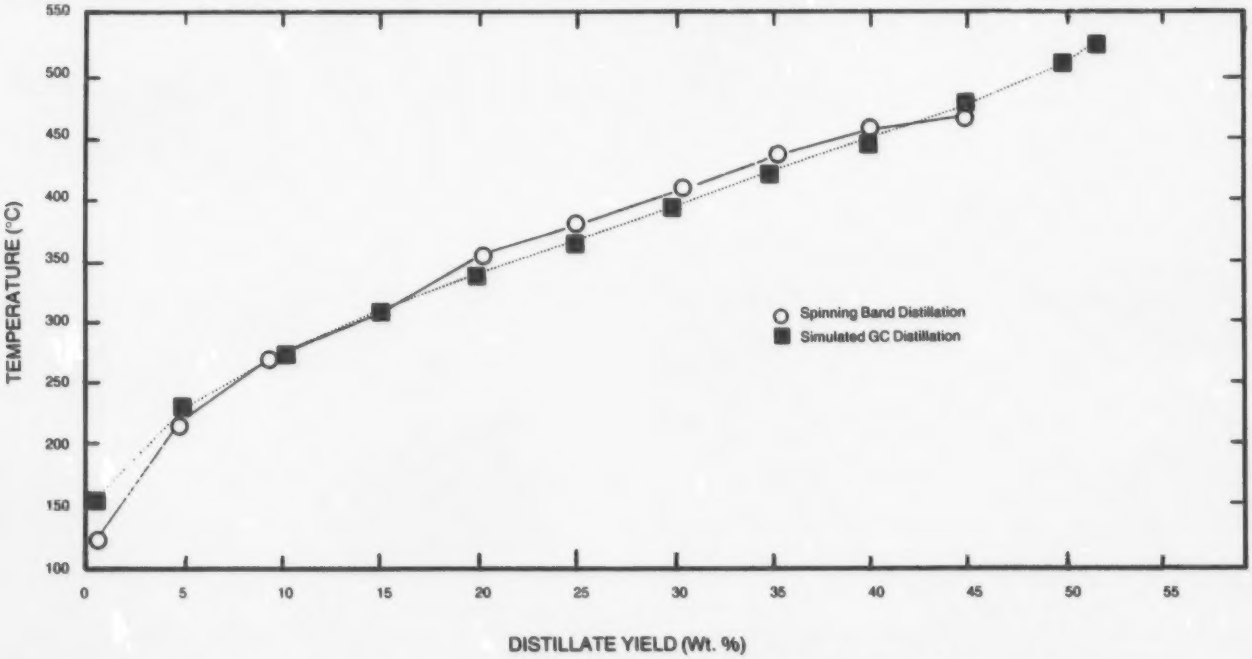

Figure 15.7: Comparison of Simulated and Spinning Band Distillation of a Suncor Coker Feed Bitumen[3]

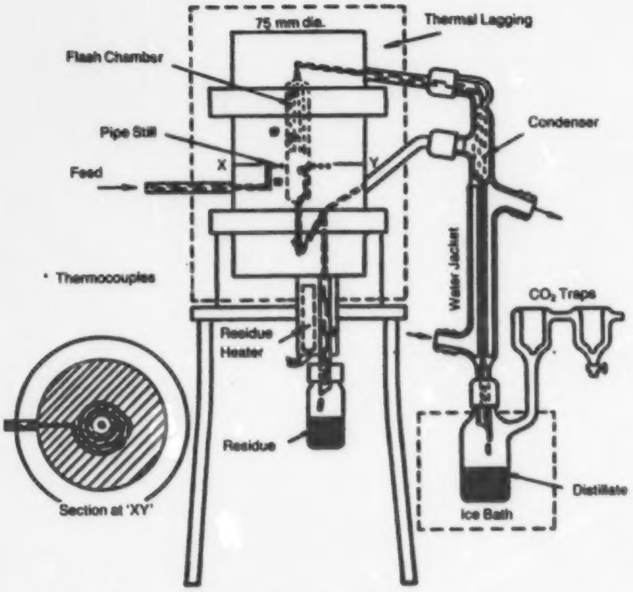

Figure 15.8: Miniature Flash Still Used by McTaggart (Copyright ASTM. Reprinted with permission.)

standard in McTaggart's study was limited to 5% of the weight of the crude to prevent detector overloading. Although this method required the least time (1½ h), it was also the least precise.

The method using four internal standards was the most accurate as judged against ASTM D2892 results. Approximately 2½ hours are required to produce a distillation curve by this method. A removable glass insert used in the injection port reduces the contamination of the column by heavy ends of the crude. Tailing of the n-paraffins of the calibration standard indicates when the column is no longer useable.

In addition to the problems in determining the percentage of sample which elutes from a GC column, errors can occur because the components of a sample can elute at a different time than n-paraffins of the same boiling point. ASTM D2887, Hickerson[6] and Southern[11] compared the observed boiling points of aromatics with literature values. Their data are reproduced in Tables 15.6 to 15.8. Southern also determined relative response factors from the flame ionization detector for several compounds using naphthalene as a reference (Table 15.9).

The ACOSA cooperative study provided an opportunity to compare GCD distillations with true boiling point distillations. The comparisons are summarized in Tables 15.10 to 15.13. None of the laboratories which conducted spinning band distillations alone were able to reach an endpoint of 524°C, an accepted endpoint in the industry. Only those labs following an unspecified high-vacuum method or ASTM D1160 were able to do so. In general, the TBP distillations provided much poorer agreement for the initial boiling point than GCD distillations. Because so few labs reported volume percent distilled at 524°C for the TBP distillations, a fair comparison cannot be made between the classes of methods at this temperature. At temperatures between IBP and 524°C, GCD appeared to be less precise for Athabasca bitumen and more precise for Lloydminster heavy oil.

Table 15.5: Comparison of Four Distillation Methods for a Kuwaiti Crude Oil[a] Each range is based on four distillations. (Copyright ASTM. Reprinted with permission.)

	Distillate yield (wt. %)			
Boiling point (°C)	**Miniature flash distillation at 380°C**	**Single internal standard method**	**Four internal standard**	**ASTM D2892**
25	1.6-2.0	1.6-1.7	1.8-2.0	2.4
50	3.5-3.7	3.4-3.6	3.8-3.9	4.1
75	6.1-6.3	6.1-6.5	6.6-6.7	6.5
100	8.8-9.5	8.8-9.6	9.2-9.7	9.6
150	16.0-16.4	15.9-16.5	15.9-16.1	16.5
200	24.1-24.4	23.9-24.9	24.0-24.5	23.8
250	31.6-32.0	31.6-32.5	30.8-31.3	31.3
300	39.6-40.0	39.7-40.8	38.7-39.3	39.4
350	47.3-47.4	47.6-48.7	46.5-46.8	47.0
400	53.6-54.0	54.0-55.9	53.2-53.8	53.9
450	57.7-59.2	62.2-63.1	60.0-60.8	60.8[a]
500	61.7-62.3	68.8-70.6	66.5-67.1	67.0[a]
Yield from flash distillation, %	62.2-63.7			

[a] Vacuum Engler extension of ASTM D2892 TBP distillation

In Table 15.14, the average results from the GCD and TBP distillations are comparable, indicating the absence of a systematic error due to the choice of general method. However, when different laboratories apply the same general method to generate a distillation curve, systematic errors are evident. The data in Tables 15.10 to 15.13 indicate that laboratories tend to report consistently low, average, or high results relative to other laboratories over the full range of the distillation curve. This is clarified in Figure 15.9, where data from only four of the labs are reported. A two-sample plot for LV% = 10 (Figure 15.10) indicates that individual laboratories tend to report consistently high or low results for a variety of samples. The trend also exists, albeit not so clearly, in the two-sample plot for LV% = 35 (Figure 15.11). Incorrect pressure measurements are the most likely cause of such systematic errors.

Table 15.6: Deviations of Simulated Distillation Boiling Points from Actual Boiling Points (ASTM D2887) (Copyright ASTM. Reprinted with permission.)

	Actual BP (°C)	Deviations from actual BP	
	(760 mm)	(760 mm)	(10 mm)
Benzene	80	+3	−2
Thiophene	86	+4	+1
Toluene	111	+2	−1
p-Xylene	139	0	−2
1-Dodecene	213	0	0
Naphthalene	218	−11	−5
2, 3-Benzothiophene	221	−13	0
2-Methylnaphthalane	241	−12	−2
1-Methylnaphthalene	245	−12	−1
Dibenzothiophene	332	−32	−5
Phenanthrene	339	−35	−9
Anthracene	342	−36	−8
Pyrene	395	−48	−16
Chrysene	447	−60	[a]

[a] No data at 10 mm for chrysene.

Table 15.7: Boiling Point of Aromatic Compounds by GC Using n-Paraffins for Calibration[a] (Copyright ASTM. Reprinted with permission.)

	Boiling point		
	Observed (°C)	Literature (°C)	Deviation (°C)
Toluene	113	111	+2
Ethylbenzene	137	136	+1
o-Xylene	148	144	+4
i-Propyl-benzene	155	152	+3
Mesitylene	164	163	+1
Sec-butyl-benzene	174	169	+5
Pseudocumene	174	169	+5
p-Cumene	179	182	−3
Durene	198	197	+1

Table 15.8: Comparison of Literature Boiling Points (BP) and Boiling Points Calculated from a Run Using Straight-Chain Hydrocarbon Standards (Reprinted with permission from Anal. Chem. 1984, 57, 303-308. Copyright 1984, American Chemical Society.)

	Literature BP (°C)	Calculated BP[a] (°C)	Deviation (°C)
Naphthalene	218	207	−11
Biphenyl	360	361	+1
Fluorene	294	278	−16
Anthracene	340	311	−29
Fluoranthene	375	351	−24
Pyrene	393	357	−36
Methylpyrene	410	368	−42
Chrysene	448	384	−54
Benzofluoranthene	480	427	−54
Benzopyrene	495	433	−62

[a] Average of 10 runs.

Table 15.9: Relative Response Factors for Various Compounds Using Naphthalene as a Reference (Reprinted with permission from Anal. Chem. 1984, 57, 303-308. Copyright 1984, American Chemical Society.)

	BP (°C)	Relative response factor[a]
Naphthalene	218	1.0
Biphenyl	260	0.96
Fluorene	294	0.97
Phenanthrene	339	0.97
Fluoranthene	375	1.04
Pyrene	393	0.87[b]
Chrysene	448	0.95
Benzopyrene	495	0.87[c]

[a] Average of 12 runs.

[b] Unresolved peak. Relative response factor on unresolved peak was 1.11.

[c] Relative response factor was concentration dependent.

In Figures 15.12 to 15.14, similar plots prepared for GCD data again indicate systematic rather than random error as the dominant source of variability between labs. Calibration of retention times rather than response factors is probably the major source of error in GCD. Note that the GCD data range increases dramatically at the higher temperatures (Tables 15.11 and 15.13).

Table 15.10: TBP Distillation Results from the ACOSA Cooperative Study – Athabasca Bitumen

Lab #	1 Spinning band	2 Spinning band	3 Spinning band	4 Spinning band + D1160	5 D2892 + HIVAC	6 HIVAC	7 HIVAC	8 D1160	9 D1160	Average temperature (°C)	Std. dev. (°C)	Range (°C)
Distillate yield (Vol %)	Temperature (°C)											
IBP	174	33[a]		142	133	158	169	164	110	150	23	110-174
5%	236	220	224	231	236	231	238	258	250	236	12	220-258
10%	286	269	278	279	291	305	286	297	300	288	11	269-305
15%	325	306	315	316	333	324	332	334	337	325	10	338-334
20%	350	338	345	348	366	375	351	363	371	356	12	388-375
25%	375	366	375	376	394	401	385	388	401	385	12	366-401
30%	414	394		412	430	430	407	412	430	416	13	394-430
35%	440	418	433	428	454	460	432	436	454	439	14	418-460
40%	454	446	461	457	475	485	463	460	479	464	13	446-485
45%				493	506	509	480	482		494	13	480-509
50%						531		505				
LV% off at 450°C	37.5	40.2	38.0	36.0	34.5	33.6	38.0	38.0	33.0	36.5	2.4	33.0-40.2
LV% off at 524°C				49.4	48.8	48.3		54.4		50.2	2.8	48.3-54.4

[a] This result was not used in the average.

Table 15.11: GC Simulated Distillation Results from the ACOSA Cooperative Study – Athabasca Bitumen

Lab. #	12	1	4	10	11	6	8	16	13	14	2	7	15	Average temperature (°C)	Std. dev. (°C)	Range (°C)
Distillate yield (Vol %)	Temperature (°C)															
IBP		140	142	160		152	165	156				162		154	10	140-165
5%	225	233	226	240	214	233	243	226	244	213	220	236	210	228	11	210-243
10%	279	289	284	296	278	290	289	282	292	292	263	285	256	281	12	256-296
15%	325	329	327	334	325	332	336	324	330	314	300	320	294	322	13	314-336
20%	366	365	361	366	363	365	373	358	363	350	335	349	325	357	14	325-373
25%	406	398	393	396	396	395	405	388	392	383	368	374	357	389	14	357-406
30%	443	433	425	425	430	425	435	418	420	415	398	399	385	419	16	385-443
35%	478	464	454	458	459	453	464	446	448	444	426	423	413	449	19	413-478
40%	511	492	486	483	489	483	490	474	475	471	454	445	439	474	22	439-511
45%			521	518	515	515	515	505	502	500	480	470	463	500	20	463-521
50%								543			506	492	487	507	25	487-543
55%												518	510			
LV% off at 524°C	41.9	45.0	45.4	45.6	46.1	46.2	46.6	47.7	48.4	49.7	53.7	56.2	58.0	48.5	4.7	41.9-58.0

Table 15.12: TBP Distillation Results from the ACOSA Cooperative Study – Lloydminster Heavy Oil

Lab #	1 Spinning band	2 Spinning band	3 Spinning band	4 Spinning band + D1160	6 HIVAC	7 HIVAC	8 D1160	9 D1160	Average temperature (°C)	Std. dev. (°C)	Range (°C)
Distillate yield (Vol %)	Temperature (°C)										
IBP	89			40	100	115	167	40	92	48	40-167
5%	210	180	188	194	220	225	218	184	202	18	180-225
10%	249	225	242	240	272	269	260	240	250	16	225-272
15%	281	265	274	272	302	298	288	288	284	13	265-302
20%	307	298	302	298	326	325	320	332	314	14	298-326
25%	331	329	332	322	355	350	346	32	342	16	322-355
30%	356	356	360	347	384	382	374	406	371	19	347-384
35%	381	384	389	375	413	409	402	435	398	20	375-413
40%	424	409		405	444	435	433	460	430	19	405-444
45%	450	431	452	439	474	460	462	484	456	17	431-474
50%		454		475	500	481	492		480	18	454-500
55%		475		514	525	512	523		510	20	475-525
60%		503									
LV% off at 450°C	44.4	49.1	44.9	45.0	41.0	43.0	42.9	38.0	43.5	3.2	38.0-49.1
LV% off at 524°C				55.7	55.0		55.6		55.4	0.4	55.0-55.7

Table 15.13: GC Simulated Distillation Results from the ACOSA Cooperative Study – Lloydminster Heavy Oil

Lab. #	12	14	4	1	10	8	6	11	13	16	2	7	15	Average temperature (°C)	Std. dev. (°C)	Range (°C)
Distillate yield (Vol %)	Temperature (°C)															
IBP			99	162[a]	105		104			105		116		106	6	104-116
5%	201	205	199	200	209	210	205	190	207	199	215	209		204	7	190-215
10%	242	247	245	248	252	250	249	229	250	244	250	249	230	245	7	229-254
15%	270	287	280	284	288	287	284	269	285	278	282	281	265	280	8	265-295
20%	320	324	314	316	323	324	319	307	315	315	315	309	296	315	8	296-330
25%	355	358	346	349	352	356	350	344	345	348	345	335	322	351	10	322-360
30%	391	390	378	381	380	387	381	380	375	378	376	364	348	378	11	348-391
35%	425	422	412	415	411	418	413	412	405	408	405	390	375	408	13	375-425
40%	460	453	443	445	439	450	442	445	435	438	434	417	402	439	15	402-460
45%	493	483	474	473	468	477	471	475	462	467	461	442	430	467	16	430-493
50%		511	508	502	503	507	503	504	490	496	489	470	458	495	16	458-511
55%					540				500		515	496	487	510	19	487-552
LV% off at 524°C	49.6	51.7	52.1	52.5	52.6	52.7	53.1	53.8	55.4	55.3	56.8	59.7	61.0	54.3	3.2	49.6-61.0

[a] This result was not used in the average.

Table 15.14: Average GCD vs. TBP Distillation Data from the ACOSA Cooperative Study

Athabasca bitumen			Lloydminster heavy oil		
Volume %	GCD °C	TBP °C	Volume %	GCD °C	TBP °C
IBP	154	150	IBP	106	92
5	228	236	5	204	202
10	281	288	10	245	250
15	322	325	15	280	284
20	357	356	20	315	314
25	389	385	25	351	342
30	419	416	30	378	371
35	449	439	35	409	398
40	474	464	40	439	430
45	500	494	45	467	456
50	507		50	495	480
			55	510	510
LV% @ 524°C	48.5	47.9	LV% @ 524°C	54.3	55.4

High Temperature GC Distillations

In GC distillations the nonpolar silicone gum stationary phase tends to bleed from the support in conventional packed columns at temperatures above 370 to 380°C. A recent development, high temperature GC distillation, offers the possibility of extending the range of the GCD curve for bitumens and heavy oils. Trestianu and co-workers described an automatic simulated distillation of heavy fractions up to 800°C by capillary gas chromatograph.[12] They found that a glass column coated with a thin film of a polar silicon was stable up to 430°C, and that compounds eluted at a column temperature approximately 100°C lower than the temperature of a packed column. In combination, these factors contributed to an endpoint of n-C_{120} or approximately 800°C. Low molecular weight polyethylenes (Polywax 655 and 1000) were used for the conversion of retention time to boiling point. Glinzer, on the other hand, extended the n-paraffin calibration curve by using low-molecular-weight polynuclear aromatics.[4] Samples were injected directly onto the column rather than into an injection port to prevent broadening of the area of the chromatogram representing components boiling above 550°C.

The method described by Trestianu extended the final boiling point which could be estimated for a sample. It did not provide for the estimation of the percent residue above 800°C in a sample, although it would appear that the strategy discussed in the proposed ASTM method could be employed, perhaps using internal standards of relatively high molecular weight. Nevertheless, good agreement between the capillary and packed column methods was reported for a residue with a boiling point range from 460 to 650°C up to the limit of the packed column (Figure 15.15). The accuracy of the capillary method was determined by analyzing a mixture of 30% internal standard (a 300 to 350°C petroleum fraction) with 70% residue. The boiling point distribution curve of the residue, calculated from the curve for the mixture with the internal standard mathematically subtracted out, deviated by a maximum of 0.3°C at any temperature from the curve for the residue alone. In a separate test, a sample consisting of five known petroleum fractions was analyzed. The capillary data agreed well with the known composition of the sample (Table 15.15).

The capillary method has been used to identify the cutpoint between a distillate and residue produced by short path distillation at an AET which could not have been identified using a conventional column (see Figure 15.16). Figure 15.17 shows the overlap between the distillate and residue fractions.

Table 15.15: Comparison Between the Theoretical and Experimental Composition of a Composite Sample Containing Different Petroleum Fractions (Reprinted with permission from J. High Res. Chromat. and Chromat. Comm. 1985, 8, 771-781.)

		Composition	
Fraction	Boiling point range (°C)	Theoretical (wt. %)	Found (Area %)
1	200-250	19.4	20.3
2	300-350	19.3	19.7
3	400-420	19.3	18.6
4	500-525	22.8	23.4
5	630+	19.2	18.0

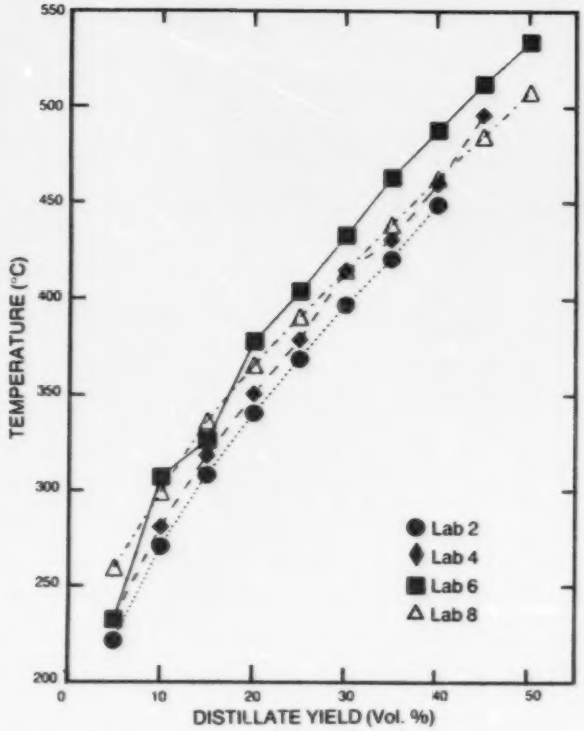

Figure 15.9: Comparison of TBP Distillation Curves for Athabasca Bitumen from Selected Laboratories in the ACOSA Cooperative Study

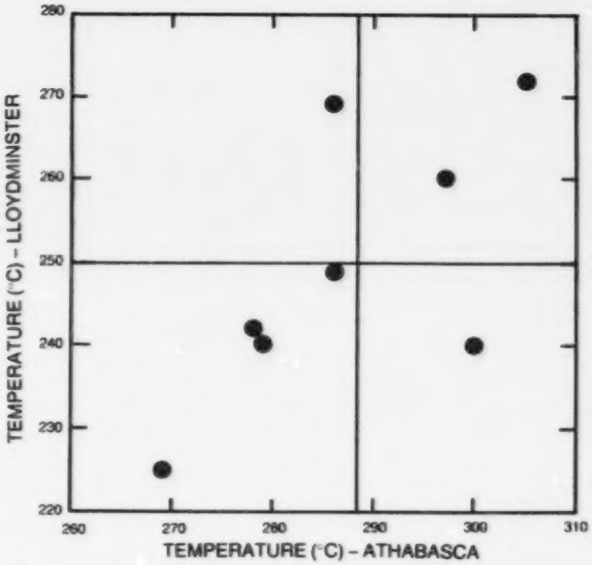

Figure 15.10: Two-Sample Plot from the ACOSA Cooperative Study for LV Equals 10% (TBP Distillation)

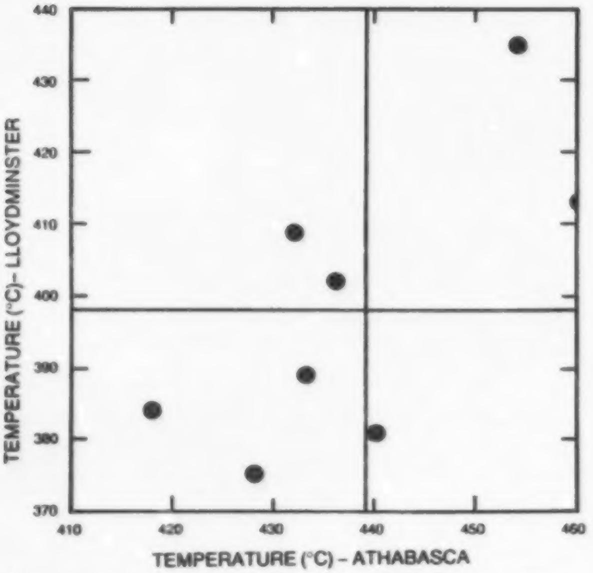

Figure 15.11: Two-Sample Plot from the ACOSA Cooperative Study for LV Equals 35% (TBP Distillation)

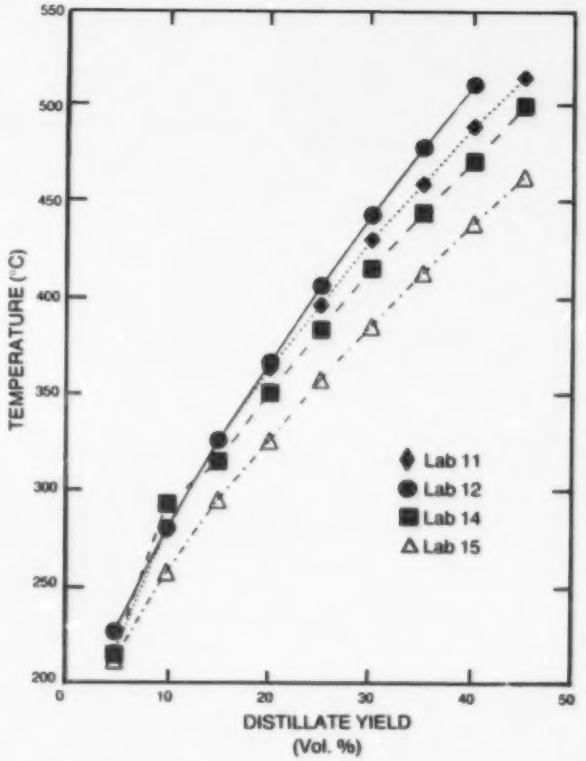

Figure 15.12: Comparison of GCD Curves for Athabasca Bitumen from Selected Laboratories in the ACOSA Cooperative Study

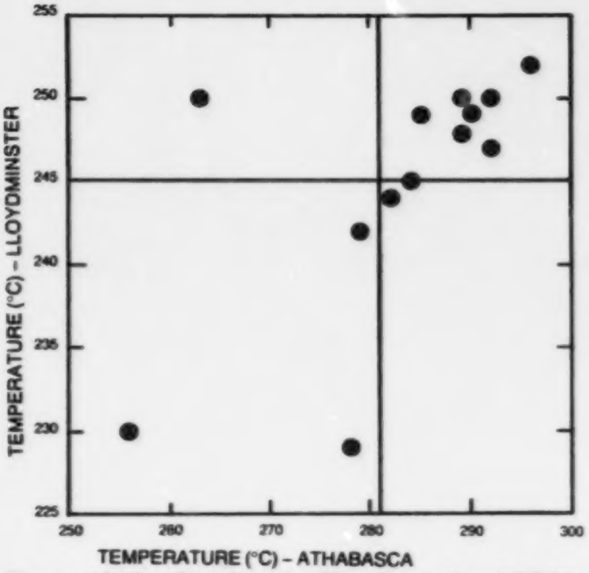

Figure 15.13: **Two-Sample Plot from the ACOSA Cooperative Study for LV Equals 10% (GCD)**

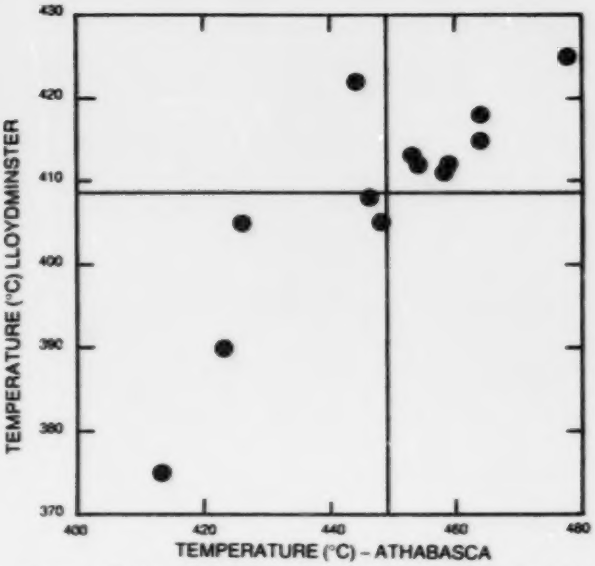

Figure 15.14: **Two-Sample Plot from the ACOSA Cooperative Study for LV Equals 35% (GCD)**

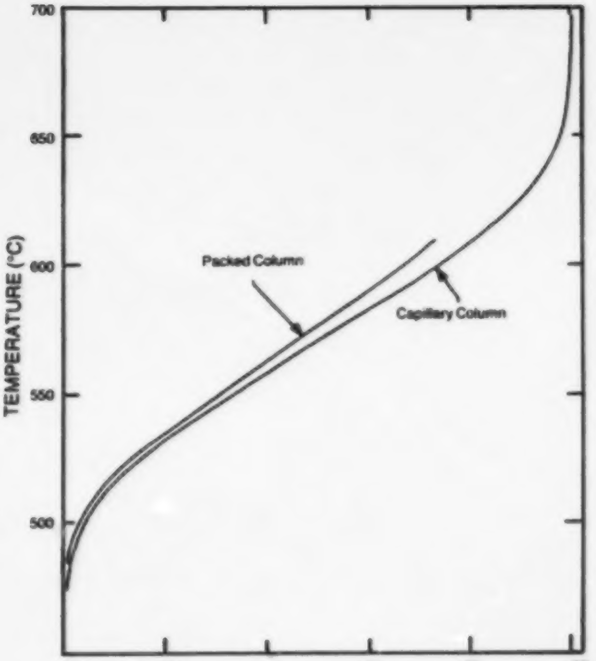

Figure 15.15: **Distillation Curves for a Petroleum Fraction (460 to 650°C) on Packed and Capillary Columns** (Reprinted with permission from J. High Res. Chromat. and Chromat. Comm. 1985, 8, 771-781.)

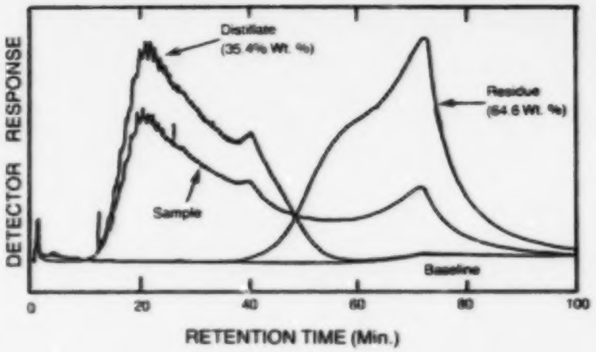

Figure 15.16: **Elution Profile using Capillary GC of the Sample, Distillate and Residue from a Short Path Distillation** (Reprinted with permission from J. High Res. Chromat. and Chromat. Comm. 1985, 8, 771-781.)

SUMMARY

At the present time there is a high level of activity in the area of actual and simulated distillations. ASTM subcommittees are either conducting cooperative studies or ballotting to revise ASTM D1160 and ASTM D2-P167. Equipment for short path distillations is now available for producing fractions from heavy crudes, but the exact cutpoints of distillates and residues above 550°C have been determined only recently by capillary chromatography.

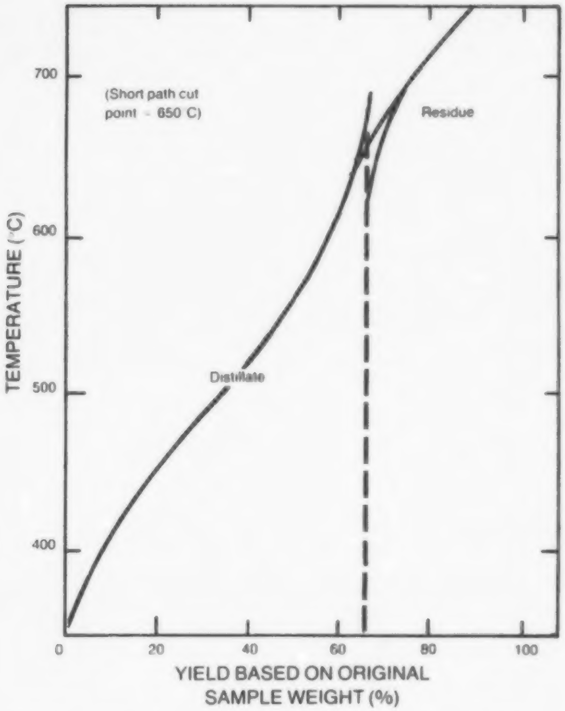

Figure 15.17: Distillation Curves using Capillary GC of the Distillate and Residue from a Short Path Distillation. The curves allow evaluation of the true boiling point (625°C) corresponding to a short path distillation cutpoint under vacuum at 325°C. (Reprinted with permission from J. High Res. Chromat. and Chromat. Comm. 1985, 8, 771-781.)

Numerous researchers have been able to establish good correlations between various methods within their own laboratories. These correlations were confirmed in the ACOSA study when the averages of all of the GCD results correlated with the average of the TBP results. There is, however, considerable variation between individual laboratories, indicating that much more work is required to standardize the methods. In the absence of precision statements in the ASTM D-2 proposed method, the ACOSA study did provide an estimate of reproducibility.

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Chapter 16: BOTTOM SEDIMENT AND WATER

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BOTTOM SEDIMENT AND WATER

DEFINITION

Bottom sediment and water (BS&W) are the solids (sediment) and free water in a crude oil or emulsion.

SIGNIFICANCE

The maximum permissible level of BS&W in crude oils in most pipelines is 0.5 vol%. Sediment in refinery feedstocks must be minimized as it deposits in distillation units and process piping.

BS&W tests are used during in-situ recovery processes to estimate the composition of produced fluids as a means of process control. Demulsification is also monitored by BS&W tests.

Crude is purchased on a dry basis so an accurate determination of BS&W is required at all custody transfer points.

METHODS

1. ASTM D96: Water and Sediment in Crude Oils

1.1 Application

This method is used to measure water and sediment in crude oils by centrifugation.

1.2 Summary of the Method

This standard defines a primary method and two alternatives, all based upon a 1:1 dilution of the oil with a suitable solvent, usually toluene, followed by centrifugation for a volumetric measurement of the water and sediment in crude oils. The exact steps necessary to ensure all of the water and sediment is measured, depend upon the properties of the crude. For example, oils containing asphaltenes must be diluted with an aromatic solvent to ensure that organic components do not precipitate and appear as sediment. Waxy crudes may require heating and bitumens often require the addition of a demulsifier. Oils with high viscosities and finely suspended solids further complicate the test. Extensive work may be necessary to identify the test conditions that will provide an accurate BS&W measurement for a specific crude. In recognition of these problems, ASTM D96 designates a Reference Method in which water is determined by ASTM D95 (distillation) and solids by ASTM D473 (solvent extraction).

1.3 Precision

Figure 16.1 illustrates the maximum allowable difference between successive test results as specified by ASTM. Repeatability and reproducibility calculated from the Phillips cooperative study, in which five laboratories conducted duplicate tests on a California crude containing 0.2 percent volume BS&W and a Maya crude containing 0.1 percent volume BS&W as defined by ASTM D96, are also shown. The laboratories in this study did not specify the size of centrifuge tube they used.

2. ASTM D4007: Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)

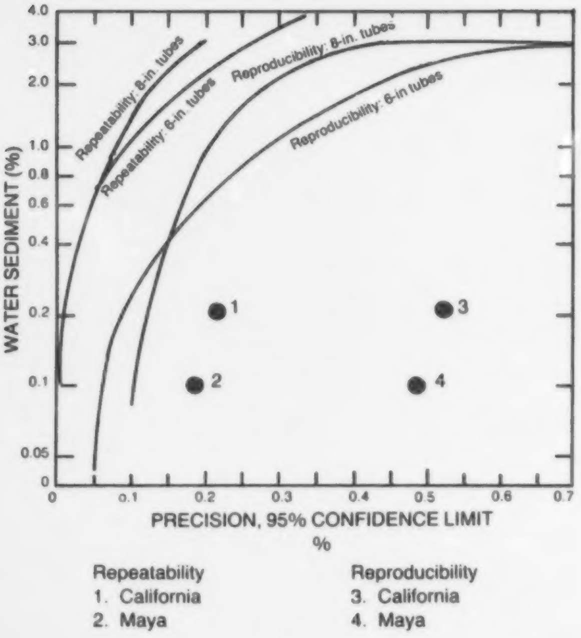

Figure 16.1: Precision Curves for ASTM D96 (Copyright ASTM. Reprinted with permission.)

2.1 Application

This method is used to measure the level of water and solids in crude oils.

2.2 Summary of the Method

Equal volumes of crude oil and water-saturated toluene, to which a demulsifier has been added, are placed in a centrifuge tube and mixed. The mixture is heated to 60°C for at least 15 minutes, remixed and then centrifuged for 10 minutes at a prescribed rate. The volume of water and solids is read. The mixture is centrifuged again for 10-minute periods until a constant reading is obtained.

When a highly accurate value for water and solids is required, ASTM D4007 recommends the use of ASTM D4006 for water and ASTM D473 for sediment.

2.3 Precision

Figure 16.2 illustrates the maximum allowable difference between successive test results as specified by ASTM. Repeatability and reproducibility calculated from the Phillips cooperative study, in which five laboratories conducted duplicate tests on a California crude containing 0.3 volume % BS&W and a Maya crude containing 0.1 volume % BS&W as defined by ASTM D4007, are also shown.

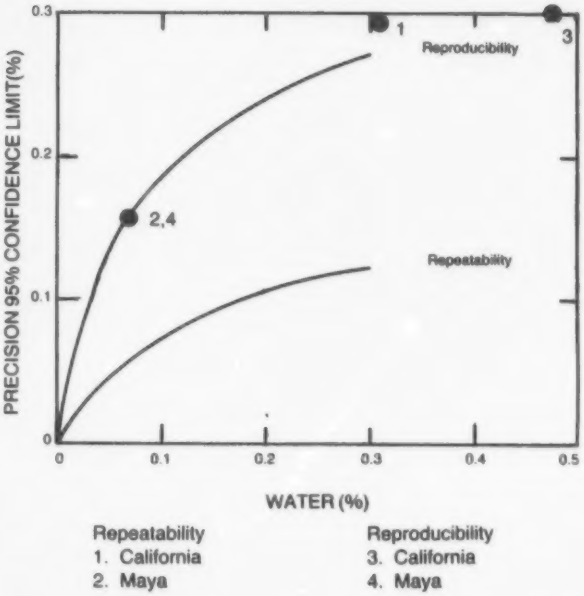

Figure 16.2: Precision Curves for ASTM D4007 (Copyright ASTM. Reprinted with permission.)

3. ASTM D95: Water in Petroleum Products and Bituminous Materials by Distillation; ASTM D4006: Water in Crude Oil by Distillation and ASTM D473: Sediment in Crude Oil and Fuel Oil by the Extraction Method

3.1 Application

ASTM D4006 and ASTM D95 describe the measurement of water in crude oil by distillation. ASTM D473 covers the measurement of sediments in oils and bitumens by extraction.

3.2 Summary of the Methods

In ASTM D4006 and D95, the test sample is mixed with a water-insoluble solvent, usually xylene or toluene, and refluxed in a flask containing boiling chips. The water co-distills with the solvent, condenses and settles into the graduated portion of a trap where it is volumetrically measured. The solvent returns to the distillation flask. A drying tube on the condenser prevents water from entering the system.

In ASTM D473, a 10-g test sample held in a refractory thimble is extracted with hot toluene until the toluene dripping from the bottom of the thimble is colorless. The thimble is dried and the residue weighed. The sample is extracted and dried again until a constant weight of residue is obtained.

3.3 Precision

	Repeatability	Reproducibility
ASTM D4006		
Phillips[a]	1.75 Vol. %	2.67 Vol. %
ASTM (above 0.1% vol.)	0.08 Vol. %	0.11 Vol. %
ASTM D473	$0.017 \pm 0.255S$	$0.033 \pm 0.255S$
where S is the average result in weight %.		

[a] From duplicate analyses by three laboratories of heavy oil emulsions containing approximately 23.5 and 14.5 vol. % water.

4. Modified Dean-Stark

4.1 Application

This method is used to measure, by extraction, the oil, water and solids content of a petroleum product or crude oil.

4.2 Summary of the Method

A 100-g sample held in a cellulose thimble is extracted in a Dean-Stark apparatus with hot toluene until the toluene droplets on the bottom of the thimble are clear. The water co-distills with the solvent, condenses, and settles into a side arm. The water is removed from the side arm and weighed. The thimble is dried and the residue weighed.

4.3 Precision

Not available for BS&W estimates.

DISCUSSION

The data in the Phillips cooperative study were poorer than applicable precision statements reported in the ASTM standards. Lack of reproducibility was attributed to the difficulty in homogenizing the initial 45-gallon samples of emulsions and subsampling which was left to the discretion of the individual laboratories.

When trying to obtain representative test samples from laboratory samples, vigorous stirring is required to disperse the constituents of the emulsion. A subsampler described by Syncrude Canada Research Ltd. (Syncrude Analytical Method 1.6) is appropriate for laboratory samples up to 2 litres.[1] Water-in-oil emulsions may require addition of diluent for efficient operation of the subsampler. However, a homogenizer of this type may produce very stable dispersions so the choice of analytical method becomes important.

A much less elaborate approach to the subsampling problem was attempted by Wong who placed a laboratory sample of tailings pond sludge in a pot (the hot water processability pot, Syncrude Analytical Method 2.1) with a drain in the bottom.[5] He allowed the sample to drain from the pot while it was stirred vigorously, and collected test samples at intervals. For sludge with an average composition of 7% bitumen, 65% water and 28% solids, the repeatabilities were 0.74, 1.22 and 0.79% respectively. Wong used the modified Dean-Stark method for these analyses. This sampling method has not been statistically evaluated for water-in-oil emulsions.

Analysts at the Alberta Research Council have also split larger samples of emulsions by draining the emulsion through several holes drilled in the bottom of one- and five-gallon containers while stirring the sample vigorously. Clearly, subsampling is a problem when such crude methods are adopted.

Obtaining representative samples of petroleum and petroleum products is the subject of ASTM D4057. Suggestions for general sampling methods (bottle, tap or thief samplers for example) and problems associated with each are described.

Graves' discussion of crude oil sampling for custody transfer described some of the techniques required to obtain representative laboratory samples.[2] He recommended that

- the best location for sampling is in a vertical line immediately downstream of a mixing system. The sampling system can be tested by injecting known amounts of water into a stream of known BS&W content (preferably 0 percent).
- the sampling tube should face upstream, and cannot be 90° to the direction of flow. Isokinetic sampling is desirable – i.e. the linear velocity through the opening in the sample probe equals the linear velocity in the pipe in front of the opening.
- the sampler should be designed to collect many small samples rather than a few large ones. For example, Graves suggested that 10,000 increments, each 1.5 mL, would be required to characterize a volume of 1 million barrels.
- the sample probe should be self-purging so that a fresh sample is always collected.

Hanzevack, Martin and Milliken reported that sampling of large volumes of crude is complicated by the separation of the oil, water and solid phases which can occur even under turbulent conditions.[3] In-line mixing is enhanced by increasing flow velocity, continuous phase viscosity or pipe length, or by decreasing interfacial tension or pipe diameter. Static in-line mixers, valves, pumps and expansion loops all assist mixing. A multipoint probe that collects several increments simultaneously permits estimation of the degree of stratification.[3]

For subsampling of composites of several Mid-east oils, Hanzevack and co-workers found that of mechanical shaking, hand shaking, mechanical mixing and recirculation through an in-line static mixture, only the latter yielded a representative test sample for BS&W. They recommended that extraction methods such as ASTM D95 and D473 provided the most accurate analysis of test samples.

Even if a representative sample is obtained, ASTM D96 and D4007 can be complicated by the presence of interfacial material in the BS&W fraction following centrifugation. For some samples the boundary between the BS&W fraction and the oil becomes clear after prolonged centrifugation; for others it does not.

In the Phillips cooperative study, some laboratories had trouble correlating their BS&W data with the volume percent water plus solids determined by Karl Fisher titration and ashing (Table 16.1). Only five laboratories conducted a BS&W, Karl Fisher, and ashing test on all samples. Even though individual laboratories had difficulties in correlating BS&W with Karl Fisher plus ash results, when all labortories' data were considered, the BS&W mean value compared well with the mean Karl Fisher plus ash values. The overall mean BS&W values from 15 laboratories for the California and Maya crudes were 0.26 vol.% and 0.10 vol.%. The overall mean water plus solids volume percent was only 0.01% lower in both cases.

Table 16.1: BS&W Compared with Solids plus Water from the Phillips Cooperative Studies

	Maya crude		California crude	
Lab	BS&W (Vol. %)	Water + solids[a] (Vol. %)	BS&W (Vol. %)	Water + solids[a] (Vol. %)
1A	0.00	0.19	0.00	0.37
B	0.00	0.24	0.00	0.42
2A	0.04	0.04	0.20	0.16
B	0.04	0.05	0.20	0.15
3A	0.05	0.06	0.15	0.23
B	0.05	0.07	0.15	0.25
4A	0.05	0.08	0.45	0.38
B	0.05	0.08	0.50	0.36
5A	0.02	0.08	0.00	0.34
B	0.02	0.08	0.00	0.32

[a] Water was determined by Karl Fisher titration. Weight percent solids was estimated by multiplying weight percent ash by 1.15. Volume percent solids was estimated by dividing weight percent solids by 2.5.

Both ASTM D96 and D4007 recognize that the centrifuge test may give low results and recommend distillation of the water and solvent extraction of this solids where accurate values are required. The modified Dean-Stark combines these two methods into one and may save time without loss of accuracy. However, it may be necessary in both ASTM D96 and the modified Dean-Stark to centrifuge the bottoms to ensure that fine solids have not passed through the thimble.

SUMMARY

The Phillips cooperative study showed that for selected samples, centrifuging can give accurate estimates of BS&W. The potential problems identified in ASTM D96 and D4007 should be considered when analyzing bitumen emulsions that may be difficult to break by physical methods.

Obtaining a representative test sample from a laboratory sample is a major problem in the determination of BS&W and there is no ASTM standard subsampling procedure that addresses this problem. Sections of ASTM D4507 may be applicable when collecting laboratory samples from bulk samples.

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Chapter 17: FLASH POINT

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FLASH POINT

DEFINITION

Flash point is the lowest temperature, corrected to a pressure of 101.3 kPa (760 mm Hg), at which the application of an ignition source causes the vapors of a sample to ignite under specified test conditions.[1]

SIGNIFICANCE

Flash point tests were introduced in England in the early 1860s as a measure of the quality of kerosene for lamps. Because kerosene is now used mainly in diesel and jet engines, flash point tests have been replaced for the most part by more appropriate tests of quality that measure volatility, viscosity, freezing point, pour point, and burning quality. Flash point tests are now used primarily to assess fire risk and to indicate the possible presence of highly volatile and flammable substances in relatively nonvolatile, nonflammable materials.

Materials with flash points below ambient or operating temperatures pose a fire hazard and transportation restrictions may apply. The International Air Transport Association (IATA) bases packaging requirements upon flash point determined by ASTM methods. The association defines a flammable liquid as "liquids or mixtures of liquids or liquids containing solids in solution or in suspension which give off a flammable vapor at temperatures of not more than 60.5°C closed-cup test or not more than 65.6°C open-cup test."[4] Some Alberta heavy oils (Wabasca, for example) would be classified as flammable liquids by this criterion.

Flash point tests are categorized as either open-cup or closed-cup. An open-cup test approximates conditions that would exist in open containers and in spills. In a closed-cup test, loss of low boiling point components to the atmosphere is restricted by a physical barrier over the surface of the cup. The test therefore permits evaluation of the flammability of sample vapors within a sealed container.

Tests are also categorized as dynamic or equilibrium. In the former, the test sample is heated and the flame is applied at specified intervals until the flash occurs. In the latter, the sample is heated to a specified temperature at which the sample and its vapors are allowed to come to equilibrium before the flame is applied. If one wishes to retest at the same or different temperatures, the test sample must be replaced and the process repeated.

The methods which follow are classified by both means. Although they do not give identical results for identical samples, they all measure the properties of materials in response to heat and flame under specified conditions.

METHODS

1. ASTM D93: Flash Point by Pensky-Martens Closed Tester (Dynamic Test)

1.1 Application

This method covers the determination of the flash point of oils, suspensions of solids, and liquids that tend to form a surface film during testing.

1.2 Summary of the Method

A 75-mL sample is heated in a closed-cup at 5°C/min and stirred at 90 to 120 rpm. At 0.5°C-intervals, stirring is ceased and the vapors are tested with a flame. This process is repeated until a flash is observed.

1.3 Precision

	Repeatability (°C)	Reproducibility (°C)
ASTM D93		
Flash point below 220°C	2	3.5
Flash point above 220°C	5.5	8.5
Phillips[a]		
California heavy oil	3	59
Maya crude	3	8

[a] From duplicate analyses by eight laboratories of a California heavy oil with a flash point of 75°C and a Maya crude with a flash point of 30°C.

2. ASTM D3828: Flash Point by Setaflash Closed Tester (Equilibrium Test)

2.1 Application

The Setaflash closed tester may be used to determine either the actual flash point of a sample or if a product will or will not flash at a specified temperature. This method is appropriate when only small quantities of sample are available.

2.2 Summary of the Method

In the flash/no-flash test, a 2-mL test sample is transferred into a heated cup which is maintained at the specified temperature. After equilibrium is reached a flame is applied and the observation recorded.

To determine the flash point, a fresh sample is placed in the cup and the test repeated at a temperature near the anticipated flash point. Successive tests are conducted at temperatures adjusted upwards or downwards, depending upon previous results until the flash point is established first within 5°C, then 1°C and 0.5°C, if necessary.

2.3 Precision

Range	Repeatability (°C)	Reproducibility (°C)
20-70°C	0.5	$0.03(M+29)$
above 70°C	$0.022M^{0.9}$	$0.083M^{0.9}$

where M is the mean of two results.

3. ASTM D56: Flash Point by Tag Closed Tester (Dynamic Test)

3.1 Application

This method covers the determination of the flash point of liquids with a flash point below 93°C, and a viscosity below 5.5 cSt at 40°C or 9.5 cSt at 25°C.

3.2 Summary of the Method

A 50-mL test sample is measured into a cup immersed in a water or water-glycol bath. The sample is heated at a rate of 1°C/min and tested with a flame every 0.5°C until a flash is observed.

3.3 Precision

Range	Repeatability (°C)	Reproducibility (°C)
Below 13°C	1.1	3.3
10 to 59°C	1.1	2.2
60 to 90°C	1.7	3.3

4. IP170: Flash Point by the Abel Apparatus (Dynamic Test)

4.1 Application

This method is used to determine the closed-cup flash points of petroleum products having flash points between −18°C and 71°C.

4.2 Summary of the Method

A 75-mL test sample, stirred at 30 rpm, is heated in a closed-cup at 1°C/min. A test flame is applied to the cup every 0.5°C until a flash is observed. Stirring is ceased before each application of the flame.

4.3 Precision

Repeatability (°C)	Reproducibility (°C)
1	1.5

5. ASTM D92: Flash and Fire Points by Cleveland Open Cup (Dynamic Test)

5.1 Application

This method is used to determine the flash point and the fire point of any petroleum product except fuel oils and those having an open cup flash below 79°C. The fire point is the temperature at which application of a test flame causes the sample to burn for at least 5 seconds.

5.2 Summary of the Method

A 30-mL test sample is heated in an open cup, without stirring, at 5°C/min. At 2°C-intervals a small test flame is passed across the cup until a flash is observed. Heating and testing maybe continued to determine the fire points.

5.3 Precision

	Repeatability (°C)	Reproducibility (°C)
Flash point	8	17
Fire point	8	14

6. ASTM D1310: Flash Point of Liquids by Tag Open-Cup Apparatus (Dynamic Test)

6.1 Application

This method covers the determination of flash and fire points of liquids having flash points between −18 and 245°C and fire points up to 290°C.

6.2 Summary of the Method

A 100-mL sample is heated in an open cup without stirring at 1°C/min and tested with a flame at 1°C-intervals to determine the flash point. The fire point may be determined by continued testing after the flash is observed.

6.3 Precision

Range	Repeatability (°C)	Reproducibility (°C)
−18 to 93°C	2.2	4
93 to 165°C	5.0	7
Viscous liquids which form a surface film	5.0	13.3

Each result is the mean of three determinations.

DISCUSSION

Sample Handling

Most flash point methods specify that samples should not be heated before testing above a temperature 10 to 20°C below the expected flash point. If the real flash point is lower than expected, and the sample handling procedures were faulty in retrospect, a new laboratory sample should be obtained for subsampling and testing.

Most of the methods also state that plastic bottles are inappropriate containers. Light components can diffuse through the walls causing erroneously high results. Samples should be stored in full tightly-sealed containers, kept cool and subsampled while they are still cool.

To demonstrate the sensitivity of flash point to the level of low boiling point components on a sample, analysts at the Alberta Research Council prepared mixtures of reagent-grade toluene and Syncrude's coker feed bitumen.[7] The flash point decreased from 180°C to 156°C after addition of just 0.7% toluene to the bitumen. The results in Table 17.1 illustrate both the need to properly store samples and the applicability of the test for identifying the presence of flammable contaminants in non-flammable materials.

Parameters Affecting Flash Point Values[5]

Flash point values may differ between testers of different designs. Although in-house testers can be built easily and economically,[8] their use is not recommended when legal and financial implications are possible. Even within one design, the recommended sample size should be tested because the volume of air space above the sample surface can influence the observed flash point. Test flames which are too large will result in erroneously low flash points.

The rate of temperature increase also influences the flash point value. At higher rates, thermal lag becomes more evident and erroneously high flash points will be reported.

Flash point testers can be standardized using pure compounds specified in ASTM standard methods. ASTM D56 and ASTM D3828, which describe the determination of flash points using Tag and Setaflash closed-cup testers, specify acceptable ranges of the flash point of p-xylene. ASTM D1310, which describes the Tag open-cup tester, recommends the use of n-heptane, p-xylene, isopropyl alcohol and diethylene glycol to calculate correction factors.

Barnard and Lance patented a method of preparing standards for the flash point test.[2] Two stable liquids are selected with flash points bracketting the desired value. The liquids must also have similar vapor pressures, molecular weights, structures and functionalities to prevent changes in the flash point caused by partial evaporation of the mixture. Barnard and Lance did not, however, specify pairs of liquids which satisfy these criteria. The flash point of each liquid is determined and the composition of the mixture having the desired flash

Table 17.1: Relationship between Flash Point (ASTM D92) and Percent Toluene in a Bitumen-Toluene Mixture[7]

Toluene (%)	Flash point (°C)
0	180
0.3	176
0.7	156
1.9	140
5.2	100
6.8	80
7.4	36

Table 17.2: Comparison of Setaflash Equilibrium Data to Setaflash Dynamic Data[3] (Copyright ASTM. Reprinted with permission.)

Sample	Flash point (°C)	
	Equilibrium (IP-303)	Dynamic (D3243-76)
No.5 (n-Nonane)	32.2	32.7
No.6 (n-Decane)	48.3	49.4

Table 17.3: Flash Test Data for Jet Fuels. Summary of Data from TCC (ASTM D56), PM (ASTM D93), Abel (IP-170) and (Setaflash ASTM D3828) (from Ref. 3) (Copyright ASTM. Reprinted with permission.)

Method	Comment on flash point level
D3828, Seta	1.7°C lower than TCC 1.7°C lower than PM equivalent to Abel
IP-170, Abel	1.7°C lower than TCC 2.2°C lower than PM equivalent to Seta
D56, TCC	1.7°C higher than Abel 1.7°C higher than Seta 1.1°C lower than PM
D93, PM	1.1°C higher than TCC 2.2°C higher than Abel 1.7°C higher than Seta

is interpolated assuming a straight-line relationship between flash point and composition. The procedure is repeated for mixtures more closely bracketing the desired flash point until the desired standard mixture is defined.

Flash point values are corrected to standard pressure by:

$$\text{Corrected flash point} = C + 0.25(101.3-p)$$

where C is the observed flash point in degrees celsius and p is the ambient barometric pressure in kilopascals.

Comparison of Methods

If the thermal lag effects reported by Lance and co-workers are significant, one would expect equilibrium tests to yield lower flash values than dynamic tests. Gibbons compared flash values from different methods for two n-paraffins and a variety of jet fuels and found that the differences were minor.[3] His results are summarized in Tables 17.2 and 17.3. In the Phillips cooperative study only one laboratory used an equilibrium test. No conclusions could be reached for heavy oils based on these limited data.[6] The Phillips study did demonstrate that for heavy crudes, ASTM D92, which is an open-cup test, tended to yield higher flash point values than closed-cup tests. Supporting data are summarized in Table 17.4.

Table 17.4: Results of Flash Point Tests Conducted in the Phillips Cooperative Study[4]

	Closed cup		Open cup	
	D56	D93	D3828[a]	D92
California crude blend				
No. of labs.	1	8	1	3
Mean flash point (°C)	71.9	66.9	81	108.0
Maya crude				
No. of labs.	1	8	1	3
Mean flash point (°C)	30.5	28.1	30.6	42.9

[a] An equilibrium test.

Lance and co-workers recommended the use of a Setaflash tester to determine flash points because the small sample required permits rapid equilibration of the sample and its vapors.[5] They reported standard deviations of less than 0.5°C in laboratory values determined by a single well-trained operator. They considered that operation of the tester under equilibrium conditions, which is a drawback in terms of analysis time, contributes to its superior precision compared to dynamic tests.

SUMMARY

The choice of flash point tests is often controlled by the purpose for which the data will be used. In-house methods and equipment can be used for quality control but flash points of heavy oils and bitumens for transportation purposes must be determined by an accepted standard method to meet IATA regulations. Some methods such as ASTM D92, ASTM D93 AND ASTM D1310 are too imprecise to classify materials having low flash points. Open-cup tests yield higher values than closed-cup tests.

Equilibrium tests such as ASTM D3838 afford the best precision but at the expense of increased analysis time if a good estimate of the flash point is not known. This shortcoming may be overcome by running a dynamic test to obtain an approximate equilibrium flash point value before conducting the equilibrium test.

Flash point values are extremely sensitive to light components. Proper sample handling and storage procedures are vital.

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Chapter 18: POUR POINT

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POUR POINT

DEFINITION

Pour point is the lowest temperature, expressed as a multiple of 3°C (5°F), at which an oil flows when cooled and examined under prescribed conditions.

SIGNIFICANCE

Pour point is an indicator of the suitability of a crude for pipelining. As most raw bitumens and heavy oils are too viscous for pipelining, the pour point test is usually conducted on diluted blends. It is also used as one indicator of the temperature at which an oil will flow during in situ operations. The test is applicable to many foreign bitumens which are solid at reservoir temperatures and to crudes at the well head during cold conditions.

Branched chained hydrocarbons, cyclic compounds and asphaltic substances contribute to the high pour points of bitumens and heavy oils, whereas the presence of n-paraffins above n-C_{18} contributes to the high pour points of many light crudes.

METHODS

1. ASTM D97: Pour Point of Petroleum Oils

1.1 Application

This method provides a measure of the lowest temperature at which an oil will flow under specified conditions and is intended for use on any petroleum oil or crude. The pour point test result is not necessarily an accurate prediction of the minimum temperature for in situ flow. The "pour" phenomenon is very sensitive to thermal history and physical disturbance. Under certain conditions, an oil may be fluid well below the pour point and under other conditions it may be solid above the pour point.

1.2 Summary of Method

Pour point is determined by heating a test sample in a jar to a predetermined temperature and subsequently cooling it at a specified rate. The test is started at a temperature which is a multiple of 3°C (5°F) and is approximately 12°C above the expected pour point. The test jar is tilted to a horizontal position. If the oil flows within 5 seconds of tilting, the sample is cooled and the test repeated at a temperature 3°C lower. The pour point is then the temperature at which no flow is first observed plus 3°C (i.e. the lowest test temperature at which the oil flows).

1.3 Precision

	Repeatability	**Reproducibility**
ASTM	3°C (5°F)	6°C (10°F)
Phillips Round Robin[a]	3°C (5°F)	12°C (20°F)

[a] From duplicate analyses by twelve laboratories of a California heavy oil blend with a pour point of -9°C and a Maya crude with a pour point of -12°C.[2]

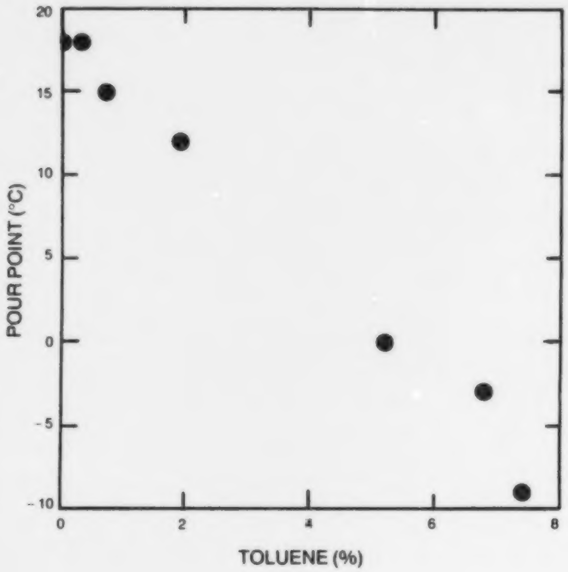

Figure 18.1: Pour Points of Mixtures of Athabasca Bitumen and Toluene

DISCUSSION

In general, oils have either a viscosity-related pour point or a wax-related pour point. Many conventional paraffinic crude oils have relatively high pour points which occur while the oil still has a low viscosity. Paraffin wax crystals precipitate from the oil and form a solid matrix. However, most bitumens and heavy oils of Alberta contain few n-paraffins so their pour points are more a result of high oil viscosities.

The thermal history of the sample should be known as it will affect the pour point. If the thermal history is not known or if the sample has been heated above 46°C (115°F), the sample should be kept at room temperature for 24 hours before being tested.

The water and solids in oil sand and production samples from in situ operations must often be removed before determining the pour point of the bitumen. Residual solvent from solvent extraction procedures can affect the reported data. Helm[1] reported pour points for mixtures of bitumen and toluene (Figure 18.1). An approximately linear relationship between percent toluene and pour point was found up to 7.5% toluene. The limit of this relationship was not identified; the pour point of the pure oil should not be extrapolated beyond the freezing point of toluene.

The repeatability of the Phillips cooperative study met the requirements described in ASTM D97, but the reproducibility was much poorer. Many labs also reported pour points which were not multiples of 3°C (5°F).

SUMMARY

ASTM D97 is the only available method for determining the pour point of bitumen and heavy oil. Highly variable pour point values will result if the test procedure is not followed rigorously.

A relationship between viscosity and pour point of bitumen is generally thought to exist but no confirming data are available. There is also no available data that describes the effect of thermal history on the pour point of a sample.

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Chapter 19: SOFTENING POINT

Contributors

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SOFTENING POINT

DEFINITION

At ambient temperatures, some bitumens are brittle solids rather than liquids. They do not melt at a definite temperature as many solids do, but gradually soften upon heating. Softening point is defined as the temperature at which a disk of bitumen softens and sags downwards a distance of 25 mm under the weight of a steel ball under strictly specified conditions.

SIGNIFICANCE

The softening point test was originally developed to characterize distillation residues or pitches for asphalt applications. Softening point can be used to describe bitumens which cannot be characterized by pour point measurements or viscosity at lower temperatures. Bitumens containing in excess of 30% pentane insolubles are suitable candidates for this measurement.

METHODS

1. ASTM D36: Softening Point of Bitumen (Ring-and-Ball Apparatus)

1.1 Application

This method covers the determination of the softening point of bitumen in the temperature range of 30 to 200°C.

1.2 Summary of the Method

Disks of solid bitumen, prepared by a standard method, are placed on rings of specified construction and submerged in a bath. A ball is placed on the top of each disk and the bath is heated at 5°C/minute until the ball causes the disk to sag 25 mm downwards. Samples believed to have softening points below 80°C are heated in water while those having softening points above 80°C are heated in glycerin. The two baths are not interchangeable as glycerin yields higher results than water for a given sample.

Rigid adherence to sample preparation and test procedures is required to obtain repeatable data.

1.3 Precision

The precision statements below were developed by round-robin testing of pitches and asphalts. They may not apply to oil sand bitumen.

Repeatability (°C)	**Reproducibility (°C)**
1	2

2. ASTM D2398: Softening Point of Bitumen in Ethylene Glycol (Ring-and-Ball)

2.1 Application

This method covers the determination of the softening point of bitumen in the temperature range of 30 to 175°C using a ring-and-ball apparatus in an ethylene glycol bath.

2.2 Summary of the Method

The test is a duplicate of ASTM D36 except that ethylene glycol is used rather than water or glycerin.

2.3 Precision

The precision of this method was defined by round robin testing of resids, pitches and asphalts. The estimates given below may not apply to oil sand bitumens.

Repeatability (°C)	Reproducibility (°C)
2	3

SUMMARY

Bitumen in Alberta deposits is fluid enough that the softening point test is not used for characterization. However, softening point is regularly used to measure the quality of asphalts which are a major product of some bitumens. In other parts of the world, Indonesia for example, where the rock asphalt is used for road-paving without prior refining, determination of the softening point of an extracted bitumen may be appropriate.

There is little to choose between the two ASTM tests. To a layman ASTM D2398 would appear to be preferable because one bath can be used for a wider range of products than a single bath in ASTM D36. However, the asphalt industry generally uses ASTM D36 because it is more precise and, by including a choice of baths, extends the range of softening points.

GLOSSARY

GLOSSARY

Terms Used in Sampling

Bulk sampling: Sampling of a material that does not consist of discrete, identifiable, constant units, but rather of arbitrary, irregular units.

Composite: A sample composed of two or more increments.

Gross sample: (also called bulk sample, lot sample) One or more increments of material taken from a larger quantity (lot) of material for assay or record purposes.

Homogeneity: The degree to which a property or substance is randomly distributed throughout a material. Homogeneity depends on the size of the units under consideration. Thus a mixture of two minerals may be inhomogeneous at the molecular or atomic level but homogeneous at the particulate level.

Increment: An individual portion of material collected by a single operation of a sampling device, from parts of a lot separated in time or space. Increments may be either tested individually or combined (composited) and tested as a unit.

Individuals: Conceivable constituent parts of the population.

Laboratory sample: A sample, intended for testing or analysis, prepared from a gross sample or otherwise obtained. The laboratory sample must retain the composition of the gross sample. Often reduction in particle size is necessary in the course of reducing the quantity.

Lot: A quantity of bulk material of similar composition whose properties are under study.

Population: A generic term denoting any finite or infinite collection of individual things, objects, or events in the broadest concept; an aggregate determined by some property that distinguishes things that do and do not belong.

Reduction: The process of preparing one or more subsamples from a sample.

Sample: A portion of a population or lot. It may consist of an individual or groups of individuals.

Segment: A specifically demarked portion of a lot, either actual or hypothetical.

Strata: Segments of a lot that may vary with respect to the property under study.

Subsample: A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, a test portion may be a subsample of a laboratory sample.

Test portion: (Also called specimen, test specimen, test unit, aliquot.) That quantity of material of proper size for measurement of the property of interest. Test portions may be taken from the gross sample directly, but often preliminary operations such as mixing or further reduction in particle size are necessary.

This material has been adapted with permission from Analytical Chemistry 1981, *53*(8), 924A.

Terms Used in Assessing the Quality of Data

Accuracy: Degree of conformity of a measured value to the true value. Accuracy is a relative term in the sense that systematic errors or biases can exist but be small enough to be inconsequential.

Collaborative study: A concerted study undertaken by several laboratories in which specimens are analyzed in each laboratory for a property by a method which is prescribed in considerable detail. Collaborative studies are the basis for determining the accuracy and precision of analytical methods in standard methods manuals such as the ASTM and IP manuals.

Cooperative Study: A concerted study undertaken by several laboratories in which specimens are analyzed in each laboratory for a property by a method that is not prescribed. The ACOSA and Phillips studies which provided much of the data in this book, were cooperative studies.

Percent: Concentrations reported in percent throughout this book imply weight percent. Repeatabilities and reproducibilities reported in percent imply absolute percent. Volume, mole and relative percents are identified as required.

Precision: The degree to which a measurement can be repeated.

Pooled standard deviation: A weighted average of individual estimates of the standard deviation.

$$s_{pooled} = \sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)\ s_2^2 + \ldots + (n_k-1)s_k^2}{(n_1-1) + (n_2-1) + \ldots\ (n_k-1)}}$$

(see standard deviation) where n is the number of data points in each data set and s is the standard deviation of each data set.

Repeatability (D2S or D2S% index which is used throughout this book: The difference between two individual test results reported by a single analyst on two test portions of the same material that would be equalled or exceeded in the long run in only 1 case in 20 in the normal and correct operation of the method. The D2S index of precision equals 2.83 times the standard deviation of a data set, the pooled standard deviation from sets of data, or repeatability standard deviation from cooperative studies. The D2S% index describes repeatability in terms relative to the average of two measurements. ASTM C670 describes the method to derive precision statements of varying stringencies.

Reproducibility (D2S or D2S% index): The difference between two individual test results reported by two laboratories on two test portions of the same material that would be equalled or exceeded in the long run in only one case in twenty in the normal and correct operation of the method.

Round robin study: An interlaboratory study in which a single laboratory sample or set of samples is sent in turn to different participants.

Standard deviation: A measure of the scatter in a set of data which fits a Gaussian distribution.

$$s = \sqrt{\frac{(x_1-\bar{x})^2 + (x_2-\bar{x})^2 + \ldots + (x_k-\bar{x})}{k-1}}$$

where $\bar{x}$ is the overall mean and x_1 to x_k are the individual values in the data set.

Two-sample plot: A graph prepared using data from a cooperative or round robin study in which the origin is defined by the overall mean results reported for the two samples. Each laboratory's data for the two samples are plotted in relation to the origin.

Uncertainty: Same as standard deviation.

APPENDIX

APPENDIX

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